Contents

Experimental procedures and characterization data

Chemicals were purchased from Acros Organics and Sigma Aldrich, and used as received. 8-Arylated BODIPY dyes were prepared according to published literature procedures, through a water based dipyrromethane synthesis followed by oxidation and condensation.[1] Aryldiazonium tetrafluoroborate salts were synthesized via traditional literature procedures.[2] All reactions were carried out in flame dried glassware, but no special precautions were taken for the exclusion of moisture. Solvents were not dried prior to use. All reactions were carried out under a nitrogen atmosphere.

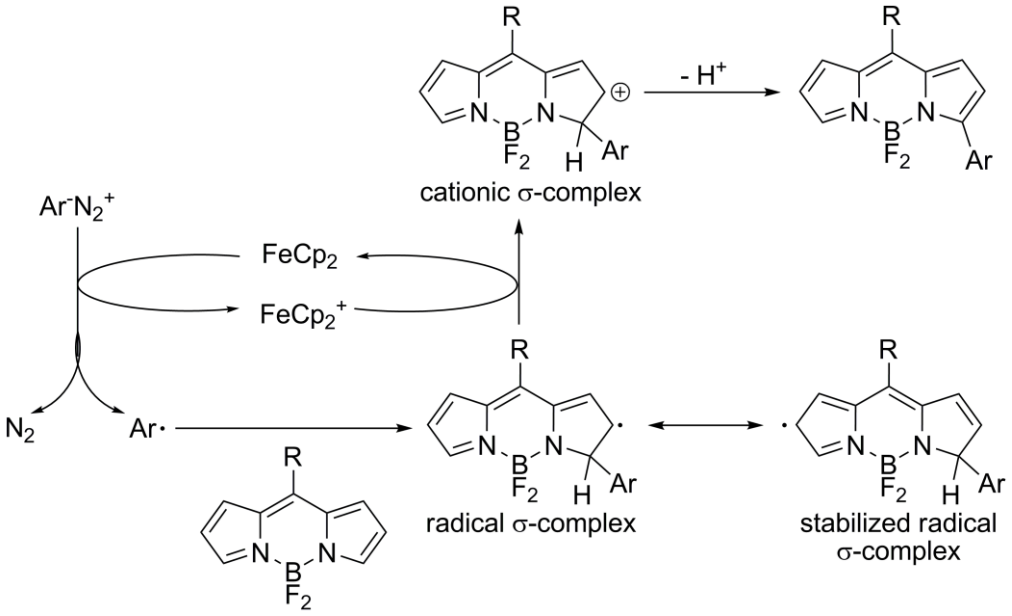
^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C. In the case of ambiguous assignments, spectra were run on a Bruker 400 or Bruker 600. ^{1}H NMR spectra in $CDCl_3$ were referenced to tetramethylsilane (0.00 ppm) as an internal standard. ^{13}C NMR spectra in $CDCl_3$ were referenced to the $CDCl_3$ (77.16 ppm) signal. ^{1}H NMR spectra in THF-d_8 were referenced to the THF-d_8 signal of 1.72 ppm. ^{13}C NMR spectra in THF-d_8 were referenced to the THF-d_8 signal of 25.31 ppm. Due to the small coupling constants in pyrroles and pyrrolic dyes, the multiplicity of the signals is often unclear. In these cases, NMR signals often appear as singlets, whereas they are not.

Mass spectra were recorded on a Hewlett-Packard 5989A mass spectrometer in E.I. mode. High-resolution mass data were obtained with a Kratos MS50TC instrument. Melting points were taken on a Reichert Thermovar and are uncorrected.

The electronic absorption spectra and absorbances were measured on a Perkin-Elmer Lambda 40 UV–vis spectrophotometer. Corrected steady-state emission spectra were recorded on a SPEX Fluorolog with temperature-controlled cell holder. Freshly prepared samples in 1-cm quartz cells were utilized to perform all UV–vis absorption and fluorescence emission measurements. For each dye in a specific solvent, multiple absorption and fluorescence spectra were recorded as a function of concentration. These experiments as a function of solvent allowed us to determine the spectral maxima [λ_{abs}(max) and λ_{em}(max)], the full width at half-height of the maximum of the absorption (fwhm$_{abs}$) and the fluorescence emission (fwhm$_{em}$) bands, and the Stokes shifts [$\Delta\bar{\nu} = 1/\lambda_{abs}(max) - 1/\lambda_{em}(max)$]. The standard uncertainty (square root of variance) on the absorption and emission maxima λ_{abs}(max) and λ_{em}(max) is approximately 1 nm. For the determination of the relative fluorescence quantum yields (Φ) in solution, only dilute solutions with an absorbance below 0.1 at the excitation wavelength were used. The measurements were performed using 10 mm optical path length cuvettes under right-angle (L-) arrangement and 'magic angle' conditions. Rhodamine 101 in ethanol (Φ_r = 0.96) and rhodamine 6G in ethanol (Φ_r = 0.95) were used as fluorescence quantum yield references.[3] The averages and standard uncertainties of Φ reported in Table 4 are computed from multiple, independent Φ

measurements (N = 2–12).[4] All spectroscopic measurements were done on non-degassed samples at 20 °C using spectroscopic grade solvents.

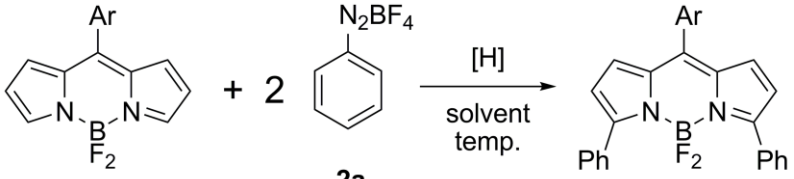
Proposed reaction mechanism



Scheme S1. Proposed aromatic homolytic substitution mechanism for the radical arylation reaction of BODIPY dyes and the stabilization of the intermediate BODIPY radical.

Optimization of the reaction protocol

Table S1. Optimization of the radical C–H phenylation of 8-(2,6-dichlorophenyl)-BODIPY.



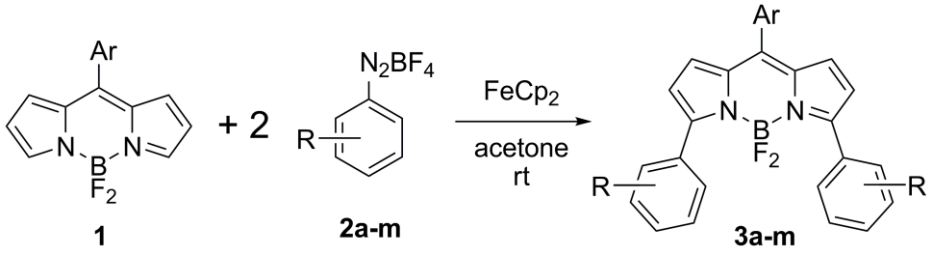
Entry	Reaction Conditions[a,b]					Yield / %[c]
	Reductant	Addition speed of reductant	Solvent	Temp-erature	Total reaction time	
1	—	—[d]	acetone	rt	20 h	trace
2	CuCl (0.10 mmol)	—[d]	acetone	rt	25 h	13
3	Cu_2S (0.05 mmol)	—[d]	acetone	rt	25.5 h	72
4	CuTC[e] (0.10 mmol)	—[d]	acetone	rt	1.5 h	63
5	$Cu(PPh_3)_3Br$ (0.10 mmol)	—[d]	acetone	rt	1.5 h	36
6	Cu(0) (0.25 mmol)	—[d]	acetone	rt	2 h	32
7	$CuCl_2$ (0.10 mmol)	—[d]	acetone	rt	18.5 h	trace
8	Hydroquinone (0.10 mmol)	—[d]	acetone	rt	21.5 h	trace
9	L-Ascorbic acid (0.25 mmol)	—[d]	acetone	rt	21 h	24

10	$FeSO_4$ (0.10 mmol)	—[d]	acetone	rt	23.5 h	trace
11	$FeCp_2$ (0.10 mmol)	—[d]	acetone	rt	20 min	41
12	$FeCp_2$ (0.05 mmol)	—[d]	acetone	rt	1 h	54
13	$FeCp_2$ (0.01 mmol)	—[d]	acetone	rt	20 h	44
14	$FeCp_2$ (0.05 mmol)	0.025 mmol/h	acetone	rt	2 h	49
15	$FeCp_2$ (0.05 mmol)	0.05 mmol/h	acetone	rt	105 min	57
16[f]	$FeCp_2$ (0.05 mmol)	0.2 mmol/h	acetone	rt	45 min	84
17	$FeCp_2$ (0.05 mmol)	0.6 mmol/h	acetone	rt	30 min	72
18	$FeCp_2$ (0.10 mmol)	0.2 mmol/h	acetone	rt	1 h	83
19	$FeCp_2$ (0.025 mmol)	0.2 mmol/h	acetone	rt	75 min	48
20[g]	$FeCp_2$ (0.05 mmol)	0.2 mmol/h	acetone	rt	45 min	67
21	$FeCp_2$ (0.05 mmol)	0.2 mmol/h	DMF[h]	rt	40 min	50
22	$FeCp_2$ (0.05 mmol)	0.2 mmol/h	MeCN	rt	2 h	32
23	$FeCp_2$ (0.05 mmol)	0.2 mmol/h	EtOH	rt	40 min	32
24	$FeCp_2$ (0.05 mmol)	0.2 mmol/h	CH_2Cl_2	rt	19.5 h	16
25	$FeCp_2$ (0.05 mmol)	0.2 mmol/h	acetone	0 °C	45 min	55

[a] Experimental conditions: 0.1 mmol 8-(2,6-dichlorophenyl)-BODIPY **1a**, 0.25 mmol of diazonium salt **2a**, reductant ($FeCp_2$ denotes ferrocene), 1 mL of solvent, stirring for the indicated time at the indicated temperature (rt = room temperature). [b] Ar is 2,6-dichlorophenyl. [c] All yields are isolated yields. [d] Reductant was added immediately. [e] Copper(I) thiophene-2-carboxylate. [f] Highest yielding condition. [g] 0.21 mmol of diazonium salt were used. [h] Dimethylformamide.

Scope of the radical reaction

Table S2. Scope of the radical C–H diarylation of the BODIPY core.[a]



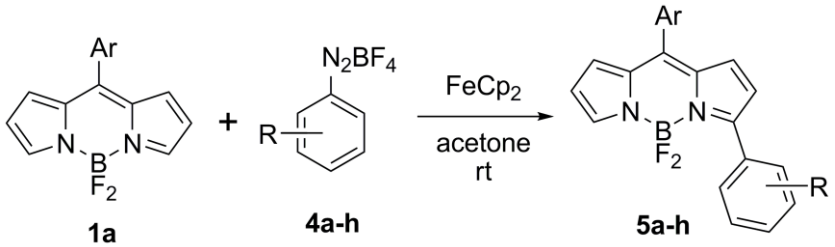
1 **2a-m** **3a-m**

Entry	Compound	Ar	R	Reaction time / min	Yield[b] of **3** / %
1	**a**	2,6-Dichlorophen-1-yl	H	45	84
2	**b**	Phenyl	H	45	60
3	**c**	Mesityl	H	45	65
4	**d**	2,6-Dichlorophen-1-yl	4-NO_2[c]	30	77
5	**e**	2,6-Dichlorophen-1-yl	3-NO_2	60	51
6	**f**	2,6-Dichlorophen-1-yl	2-NO_2[c]	40	72
7	**g**	2,6-Dichlorophen-1-yl	4-CN	40	86
8	**h**	2,6-Dichlorophen-1-yl	4-Br[c]	40	53
9	**i**	2,6-Dichlorophen-1-yl	4-COOH	45	69

10	**j**	2,6-Dichlorophen-1-yl	benzo[c]	45	54
11	**k**	2,6-Dichlorophen-1-yl	2,4,6-Me_3	150	19
12	**l**	2,6-Dichlorophen-1-yl	4-OMe	50	30
13	**m**	2,6-Dichlorophen-1-yl	4-NMe_2[d]	180	35[e]

[a] Experimental conditions: 0.1 mmol BODIPY **1**, 0.25 mmol diazonium salt **2**, 0.05 mmol $FeCp_2$ (0.2 mmol/h), 1 mL acetone (0.1 M), stirring for the indicated time at room temperature (rt). [b] Isolated yield. [c] 0.2 mmol diazonium salt and 0.04 mmol $FeCp_2$ were used. [d] $Me_{10}FeCp_2$ was used as reducing agent. [e] Isolated yield of monoarylated compound, diarylated compound is only formed in trace amount.

Table S3. Scope of the radical C–H monoarylation of 8-(2,6-dichlorophenyl)-BODIPY.[a,b]

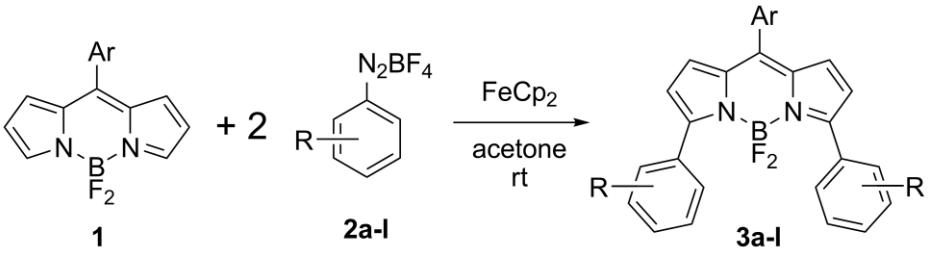


1a **4a-h** **5a-h**

Entry	Compound	R	Reaction time / min	Yield[c] of **5** / %
1	**a**	H	35	58
2	**b**	4-NO_2	35	50
3	**c**	4-CN	40	74
4	**d**	4-COOH	35	53
5	**e**	benzo[c]	40	53
6	**f**	2,4,6-Me_3	105	52
7	**g**	4-OMe	40	41
8	**h**	4-NMe_2[d]	105	26

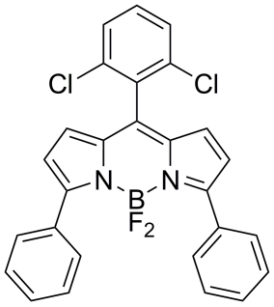
[a] Experimental conditions: 0.1 mmol 8-(2,6-dichlorophenyl)-BODIPY **1a**, 0.1 mmol diazonium salt **4**, 0.02 mmol $FeCp_2$ (0.2 mmol/h), 1 mL acetone (0.1 M), stirring for the indicated time at room temperature (rt). [b] Ar is 2,6-dichlorophenyl. [c] Isolated yield. [d] $Me_{10}FeCp_2$ was used as reducing agent.

General radical C–H diarylation procedure.



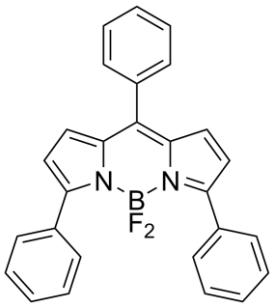
BODIPY **1** (0.1 mmol) and the aryldiazonium tetrafluoroborate salt **2a-l** (0.25 mmol) were dissolved in acetone (0.8 mL). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (9.3 mg, 0.05 mmol in 0.2 mL acetone) over 15 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

3,5-Diphenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3a).



Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and benzenediazonium tetrafluoroborate **2a** (48.0 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 2:1 (v/v)] providing a purple solid with a copper luster (41.0 mg, 84%). Data are in full accordance with the literature.[4]

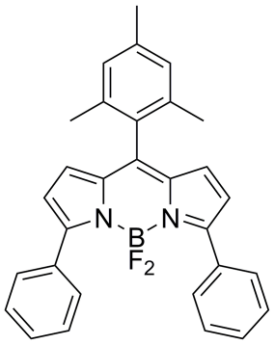
3,5,8-Triphenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3b).



Prepared according to the general procedure for the radical C–H diarylation using 8-phenylBODIPY **1b** (26.8 mg, 0.1 mmol) and benzenediazonium tetrafluoroborate **2a** (48.0

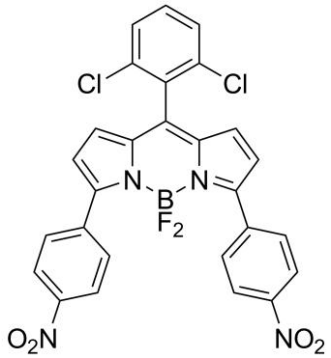
mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 2:1 (v/v), followed by silica; petroleum ether/ethyl acetate; 9:1 (v/v)] providing a dark purple solid (25.3 mg, 60%). Data are in full accordance with the literature.[4]

3,5-Diphenyl-8-mesityl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3c).



Prepared according to the general procedure for the radical C–H diarylation using 8-mesitylBODIPY **1c** (31.0 mg, 0.1 mmol) and benzenediazonium tetrafluoroborate **2a** (48.0 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 2:1 (v/v)] providing a purple solid with a green luster (29.8 mg, 65%). Mp 211 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.92-7.85 (m, 4H), 7.47-7.38 (m, 6H), 6.99 (s, 2H), 6.66 (d, 2H, *J* = 4.15 Hz), 6.55 (d, 2H, *J* = 3.95 Hz), 2.38 (s, 3H), 2.21 (s, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 158.9, 144.1, 138.7, 137.0, 136.7, 132.8, 130.5, 129.6, 129.6, 129.5, 128.4, 128.3, 120.9, 21.3, 20.3 ppm; MS (EI, *m/z*): 462; HRMS (*m/z*): calculated for $C_{30}H_{25}BF_2N_2$ 462.20789, measured 462.20927.

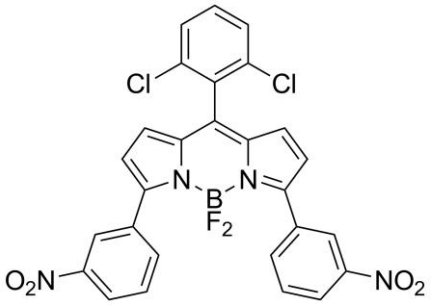
3,5-Di(4-nitrophenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3d).



Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-nitrobenzenediazonium tetrafluoroborate **2d** (47.4 mg, 0.2 mmol). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (7.44 mg, 0.04 mmol in 0.2 mL acetone) over 12 min. The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether; 1:1 (v/v), followed by silica; petroleum ether/CH_2Cl_2; 4:6 (v/v)] providing a

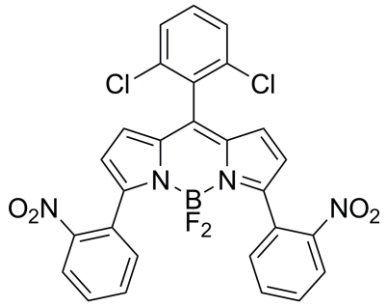
purple solid with a green metallic luster (44.4 mg, 77%). Mp 330 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.31 (d, 4H, *J* = 8.85 Hz), 8.06 (d, 4H, *J* = 8.85 Hz), 7.59-7.45 (m, 3H), 6.79 (d, 2H, *J* = 4.30 Hz), 6.71 (d, 2H, *J* = 4.30 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 157.6, 148.4, 138.1, 137.0, 135.5, 131.7, 131.3, 130.5, 130.5, 128.5, 123.7, 122.6, 122.2 ppm; MS (EI, *m/z*): 578 (100%), 579 (49%), 580 (69%); HRMS (*m/z*): calculated for $C_{27}H_{15}BCl_2F_2N_4O_4$ 578.05315, measured 578.05528.

3,5-Di(3-nitrophenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3e).



Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 3-nitrobenzenediazonium tetrafluoroborate **2e** (59.3 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether; 6:4 (v/v), followed by silica; petroleum ether/CH_2Cl_2; 4:6 (v/v)] providing a red solid (39.3 mg, 51%). Mp 148 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.69 (t, 2H *J* = 1.90 Hz), 8.37-8.24 (m, 4H), 7.65 (t, 2H, *J* = 8.00 Hz), 7.58-7.44 (m, 3H), 6.79 (d, 2H, *J* = 4.15 Hz), 6.72 (d, 2H, *J* = 4.15 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 157.4, 148.3, 136.7, 135.6, 135.5, 135.5, 135.5, 133.7, 131.7, 131.4, 130.4, 129.6, 128.5, 124.6, 121.8 ppm; MS (EI, *m/z*): 578; HRMS (ESI-TOF, *m/z*): [M + K^+] calculated for $C_{27}H_{15}BCl_2F_2KN_4O_4$ 617.0169, measured 617.0166.

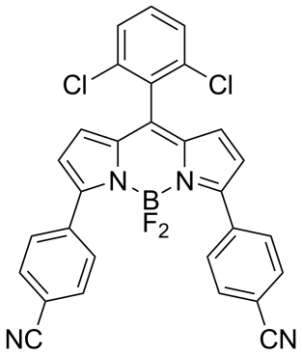
3,5-Di(2-nitrophenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3f).



Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 2-nitrobenzenediazonium tetrafluoroborate **2f** (47.4 mg, 0.2 mmol). To this reaction mixture was added dropwise, at

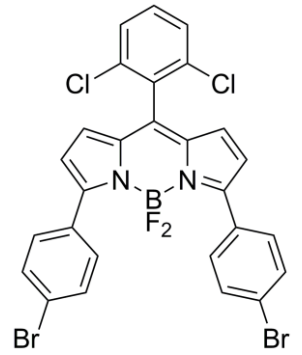
room temperature, a ferrocene solution (7.44 mg, 0.04 mmol in 0.2 mL acetone) over 12 min. The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 1:2 (v/v)] providing a red solid with a copper luster (41.9 mg, 72%). Mp: decomposition at 320 °C; ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 8.10 (d, 2H, *J* = 7.90 Hz), 7.66-7.60 (m, 3H), 7.57-7.50 (m, 4H), 7.45 (t, 2H, *J* = 8.05 Hz), 6.74 (d, 2H, *J* = 4.10 Hz), 6.41 (d, 2H, *J* = 4.15 Hz) ppm; ^{13}C-NMR: product is too insoluble to obtain a fully resolved spectrum; MS: product cannot be ionized; HRMS: product cannot be ionized.

3,5-Di(4-cyanophenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3g).



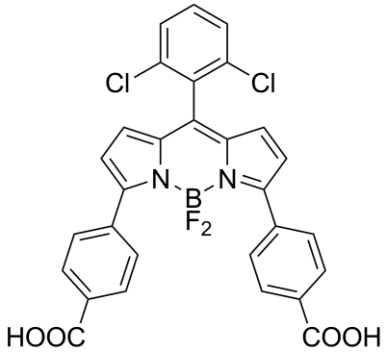
Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-cyanobenzenediazonium tetrafluoroborate **2g** (54.3 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 1:2 (v/v)] providing a dark purple solid with a green metallic luster (46.3 mg, 86%). Mp: transition at 315 °C, melting point at 345 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.00 (d, 4H, *J* = 8.65 Hz), 7.74 (d, 4H, *J* = 8.65 Hz), 7.57-7.44 (m, 3H), 6.77 (d, 2H, *J* = 4.15 Hz), 6.67 (d, 2H, *J* = 4.30 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 157.9, 136.9, 136.3, 135.6, 132.2, 131.7, 131.4, 130.3, 130.2, 130.1, 128.5, 122.0, 118.6, 113.4 ppm; MS (EI, *m/z*): 538; HRMS (*m/z*): calculated for $C_{29}H_{15}BCl_2F_2N_4$ 538.07349, measured 538.07361.

3,5-Di(4-bromophenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3h).



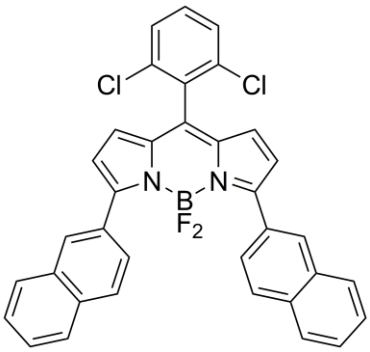
Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-bromobenzenediazonium tetrafluoroborate **2h** (54.0 mg, 0.2 mmol). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (7.44 mg, 0.04 mmol in 0.2 mL acetone) over 12 min. The crude product was purified by column chromatography [silica; petroleum ether/toluene; 2:1 (v/v), followed by silica; petroleum ether/diethyl ether; 4:1 (v/v)] providing dark purple crystals with a green luster (34.5 mg, 53%). Mp 324 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, 4H, *J* = 8.65 Hz), 7.58 (d, 4H, *J* = 8.65 Hz), 7.54-7.41 (m, 3H), 6.68 (d, 2H, *J* = 4.30 Hz), 6.60 (d, 2H, *J* = 3.95 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 158.7, 136.3, 135.7, 131.9, 131.7, 131.3, 131.2, 131.1, 131.1, 129.5, 128.4, 124.8, 121.5 ppm; MS (EI, *m/z*): 644 (38%), 646 (100%), 647 (52%), 648 (90%); HRMS (*m/z*): calculated for $C_{27}H_{15}BBr_2Cl_2F_2N_2$ 643.90402, measured 643.90721.

3,5-Di(4-carboxyphenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3i).



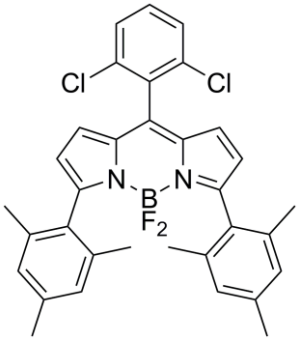
Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-carboxybenzenediazonium tetrafluoroborate **2i** (59.0 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; CH_2Cl_2/methanol/acetic acid; 94:6:0.1 (v/v/v)] providing a purple solid (40.0 mg, 69%). Mp > 350 °C; ^{1}H-NMR (THF-d_8, 300 MHz): δ 8.06 (s, 8H), 7.67-7.53 (m, 3H), 6.84 (d, 2H, *J* = 4.30 Hz), 6.80 (d, 2H, *J* = 4.35 Hz) ppm; ^{13}C-NMR (THF-d_8, 150 MHz): δ 167.2, 159.8, 137.5, 137.0, 136.3, 132.7, 132.6, 130.4, 130.4, 130.4, 130.3, 130.2, 129.3, 122.7 ppm; MS (EI, *m/z*): 576; HRMS (*m/z*): calculated for $C_{29}H_{17}BCl_2F_2N_2O_4$ 576.06265, measured 576.06637.

3,5-Di(2-naphthyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3j).



Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and naphthalene-2-diazonium tetrafluoroborate **2j** (60.5 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 2:1 (v/v), followed by silica; petroleum ether/toluene; 1:1 (v/v)] providing a dark purple solid with a green metallic luster (31.8 mg, 54%). Mp 311 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.43 (s, 2H), 8.05 (dd, 2H, J_1 = 8.65 Hz, J_2 = 1.70 Hz), 7.94-7.79 (m, 6H), 7.57-7.41 (m, 7H), 6.79-6.68 (m, 4H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 159.9, 136.4, 136.0, 133.9, 133.1, 132.3, 131.2, 130.0, 130.0, 130.0, 129.2, 129.1, 128.4, 128.0, 127.8, 127.3, 126.8, 126.4, 122.0 ppm; MS (EI, *m/z*): 588; HRMS (*m/z*): calculated for $C_{35}H_{21}BCl_2F_2N_2$ 588.11429, measured 588.11289.

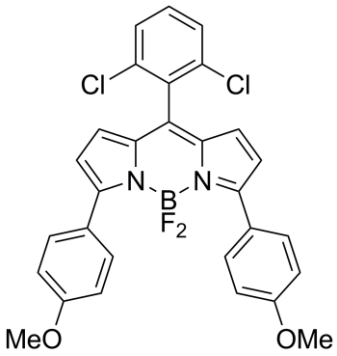
3,5-Dimesityl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3k).



Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 2,4,6-trimethylbenzenediazonium tetrafluoroborate **2k** (58.5 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 7:3 (v/v)] providing an orange solid with a green luster (11.0 mg, 19%). Mp: decomposition at 320 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.56-7.40 (m, 3H), 6.83 (s, 4H), 6.69 (d, 2H, J = 4.15 Hz), 6.24 (d, 2H, J = 3.95 Hz), 2.25 (s, 6H), 2.11 (s, 12H) ppm; ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 160.1, 138.5, 137.8, 137.4, 135.7, 134.9, 132.2, 131.1, 129.9, 129.0, 128.3, 127.7, 121.0, 21.3, 20.3 ppm; MS (EI, *m/z*): 572

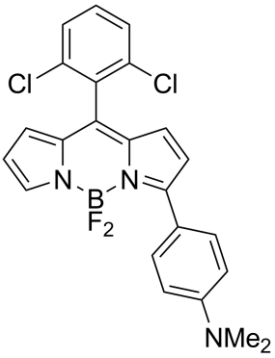
(M), 552 (M-HF); HRMS (*m/z*): calculated for $C_{33}H_{29}BCl_2F_2N_2$ 572.17689, measured 572.17554.

3,5-Di(4-methoxyphenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3l).



Prepared according to the general procedure for the radical C–H diarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-methoxybenzenediazonium tetrafluoroborate **2l** (55.5 mg, 0.25 mmol). The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether; 2:1 (v/v), followed by silica; petroleum ether/CH_2Cl_2; 1:1 (v/v)] providing a purple solid with a green luster (16.2 mg, 30%). Data are in full accordance with the literature.[4]

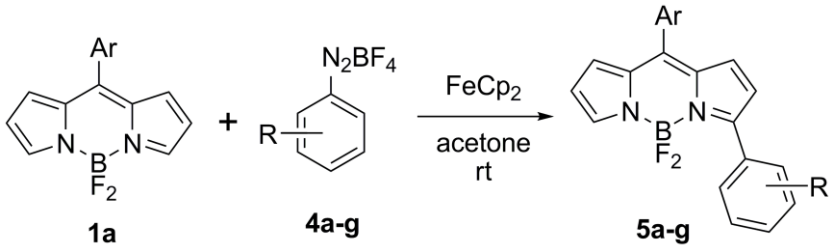
3-(4-(Dimethylamino)phenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5h).



8-(2,6-Dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-(dimethylamino)benzenediazonium tetrafluoroborate **2m** (58.8 mg, 0.25 mmol) were dissolved in acetone (0.9 mL). To this reaction mixture was added dropwise, at room temperature, a decamethylferrocene solution (16.3 mg, 0.05 mmol in 0.2 mL CH_2Cl_2) over 15 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether/triethylamine; 66:34:0.1 (v/v/v),

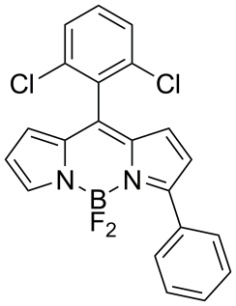
followed by silica; petroleum ether/CH_2Cl_2/triethylamine; 40:60:0.1 (v/v/v)] providing a green solid with a metallic luster (15.9 mg, 35%). Mp 200 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.10 (d, 2H, *J* = 9.25 Hz), 7.71 (s, 1H), 7.51-7.35 (m, 3H), 6.84-6.74 (m, 3H), 6.70 (d, 1H, *J* = 4.70 Hz), 6.46-6.38 (m, 2H), 3.10 (s, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 152.2, 138.8, 135.9, 132.6, 132.4, 132.2, 132.2, 132.1, 131.5, 130.9, 128.3, 124.1, 122.4, 118.5, 116.6, 111.6, 103.6, 40.2 ppm; MS (EI, *m/z*): 455 (100%), 456 (45%), 457 (68%); HRMS (*m/z*): calculated for $C_{23}H_{18}BCl_2F_2N_3$ 455.09389, measured 455.0947.

General radical C–H monoarylation procedure.



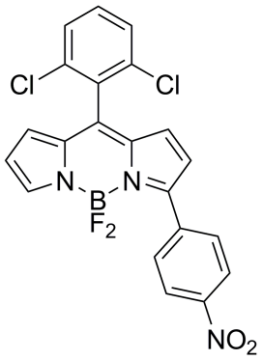
BODIPY **1a** (0.1 mmol) and the aryldiazonium tetrafluoroborate salt **4a-g** (0.1 mmol) were dissolved in acetone (0.8 mL). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (3.7 mg, 0.02 mmol in 0.2 mL acetone) over 6 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

3-Phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5a).



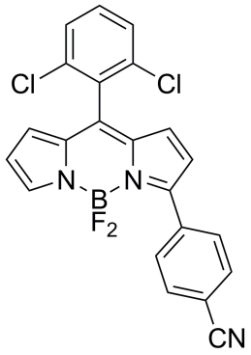
Prepared according to the general procedure for the radical C–H monoarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and benzenediazonium tetrafluoroborate **4a** (19.2 mg, 0.1 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 2:1 (v/v)] providing a red solid with a green luster (23.9 mg, 58%). Data are in full accordance with the literature.[4]

3-(4-Nitrophenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5b).



Prepared according to the general procedure for the radical C–H monoarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-nitrobenzenediazonium tetrafluoroborate **4b** (23.7 mg, 0.1 mmol). The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether; 2:1 (v/v), followed by silica; petroleum ether/CH_2Cl_2; 4:6 (v/v)] providing a purple solid with a copper luster (22.7 mg, 50%). Mp 236 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.34 (d, 2H, *J* = 8.85 Hz), 8.14 (d, 2H, *J* = 8.85 Hz), 7.96 (s, 1H), 7.56-7.41 (m, 3H), 6.78-6.72 (m, 2H), 6.69 (d, 1H, *J* = 4.15 Hz), 6.57 (d, 1H, *J* = 3.95 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 156.7, 148.3, 146.4, 140.4, 138.3, 137.1, 135.4, 135.0, 131.6, 131.4, 130.5, 130.5, 130.4, 128.5, 123.7, 121.1, 120.3 ppm; MS (EI, *m/z*): 457 (100%), 458 (43%), 459 (69%); HRMS (*m/z*): calculated for $C_{21}H_{12}BCl_2F_2N_3O_2$ 457.03677, measured 457.03817.

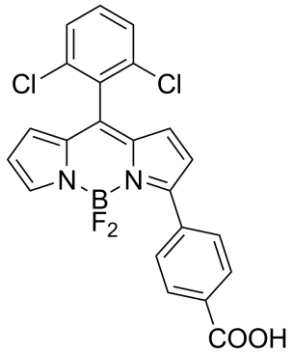
3-(4-Cyanophenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5c).



Prepared according to the general procedure for the radical C–H monoarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-cyanobenzenediazonium tetrafluoroborate **4c** (21.7 mg, 0.1 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 1:2 (v/v)] providing a purple solid with a green luster (32.5 mg, 74%). Mp: decomposition at 150 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.08 (d, 2H, *J* = 8.65 Hz), 7.94 (s, 1H), 7.77 (d, 2H, *J* = 8.65 Hz), 7.55-7.41 (m, 3H), 6.77-6.71 (m, 2H), 6.67 (d, 1H, *J* = 4.15 Hz), 6.56 (d, 1H, *J* = 4.15 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75

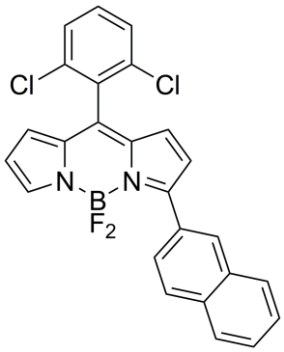
MHz): δ 157.4, 146.0, 137.0, 136.4, 135.4, 134.8, 132.2, 131.5, 131.4, 130.5, 130.2, 130.1, 130.1, 128.5, 121.0, 120.0, 118.8, 113.3 ppm; MS (EI, *m/z*): 437; HRMS (*m/z*): calculated for $C_{22}H_{12}BCl_2F_2N_3$ 437.04694, measured 437.04898.

3-(4-Carboxyphenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5d).



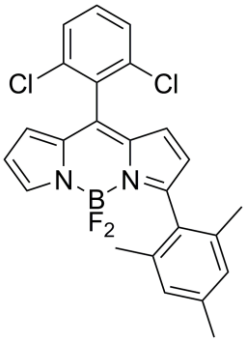
Prepared according to the general procedure for the radical C–H monoarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-carboxybenzenediazonium tetrafluoroborate **4d** (23.6 mg, 0.1 mmol). The crude product was purified by column chromatography [silica; CH_2Cl_2 to CH_2Cl_2/ethyl acetate/acetic acid; 80:20:0.1 (v/v/v)]. This was partially evaporated. Next, the solution was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness providing a purple solid with a green metallic luster (24.1 mg, 53%). Mp: transition at 232 °C, decomposition at 300 °C; ^{1}H-NMR (THF-d_8, 300 MHz): δ 8.17-8.07 (m, 4H), 7.96 (s, 1H), 7.64-7.52 (m, 3H), 6.88 (d, 1H, *J* = 4.35 Hz), 6.82 (d, 1H, *J* = 4.30 Hz), 6.73 (d, 1H, *J* = 4.15 Hz), 6.56 (d, 1H, *J* = 4.15 Hz) ppm; ^{13}C-NMR (THF-d_8, 75 MHz): δ 167.2, 160.3, 145.9, 140.0, 136.7, 136.0, 132.9, 132.6, 132.5, 131.4, 130.4, 130.4, 130.3, 130.2, 129.6, 129.3, 122.3, 120.0 ppm; MS (ESI, *m/z*): 608 ($M^+ + CH_2Cl_2 + CH_2Cl_2 - F$), 876 ($M^+ + M^+ - F - F$); HRMS (ESI-TOF, *m/z*): $[M + H]^+$ calculated for $C_{22}H_{14}BCl_2F_2N_2O_2$ 457.0488, measured 457.0483; $[M - F]^+$ calculated for $C_{22}H_{13}BCl_2FN_2O_2$ 437.0431, measured 437.0426; $[M - H]^-$ calculated for $C_{22}H_{12}BCl_2F_2N_2O_2$ 455.0342, measured 455.0350; $[M - H - CO_2]^-$ calculated for $C_{21}H_{12}BCl_2F_2N_2$ 411.0439, measured 411.0449.

3-(2-Naphthyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5e).



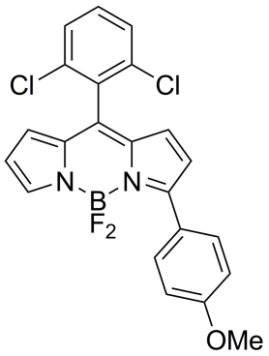
Prepared according to the general procedure for the radical C–H monoarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and naphthalene-2-diazonium tetrafluoroborate **4e** (24.2 mg, 0.1 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 2:1 (v/v)] providing a purple solid with a copper luster (24.7 mg, 53%). Mp: decomposition at 125 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.55 (s, 1H), 8.10 (dd, 1H, J_1 = 8.65 Hz, J_2 = 1.70 Hz), 8.01-7.92 (m, 2H), 7.91-7.84 (m, 2H), 7.60-7.40 (m, 5H), 6.84-6.76 (m, 2H), 6.64 (d, 1H, J = 3.95 Hz), 6.49 (d, 1H, J = 3.20 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 161.6, 143.3, 137.4, 135.6, 134.1, 133.9, 133.1, 131.9, 131.3, 131.1, 130.3, 129.3, 128.4, 128.1, 128.0, 127.8, 127.6, 126.7, 126.5, 126.5, 126.4, 122.2, 118.7 ppm; MS (EI, *m/z*): 462 (100%), 463 (43%), 464 (66%); HRMS (*m/z*): calculated for $C_{25}H_{15}BCl_2F_2N_2$ 462.06734, measured 462.06827.

3-Mesityl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5f).



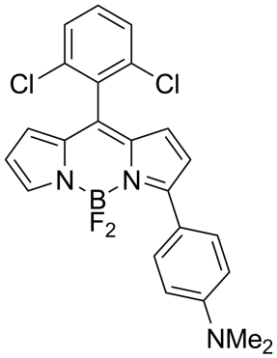
Prepared according to the general procedure for the radical C–H monoarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 2,4,6-trimethylbenzenediazonium tetrafluoroborate **4f** (23.4 mg, 0.1 mmol). The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 6:4 (v/v)] providing an orange solid with a green luster (23.8 mg, 52%). Data are in full accordance with the literature.[4]

3-(4-Methoxyphenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5g).



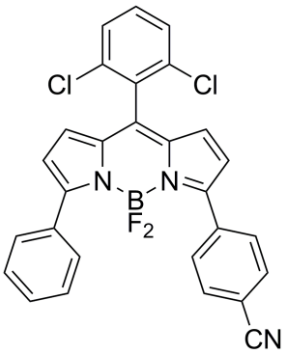
Prepared according to the general procedure for the radical C–H monoarylation using 8-(2,6-dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-methoxybenzenediazonium tetrafluoroborate **4g** (22.2 mg, 0.1 mmol). The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether; 7:3 (v/v), followed by silica; petroleum ether/diethyl ether; 2:1 (v/v)] providing dark crystals with a copper luster (18.2 mg, 41%). Data are in full accordance with the literature.[4]

3-(4-(Dimethylamino)phenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (5h).



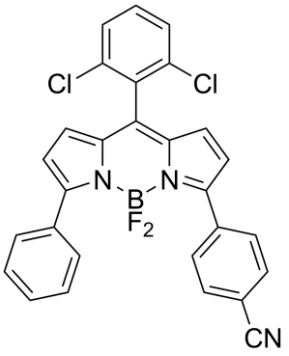
8-(2,6-Dichlorophenyl)-BODIPY **1a** (33.7 mg, 0.1 mmol) and 4-(dimethylamino)benzenediazonium tetrafluoroborate **2m** (23.5 mg, 0.1 mmol) were dissolved in acetone (0.9 mL). To this reaction mixture was added dropwise, at room temperature, a decamethylferrocene solution (6.5 mg, 0.02 mmol in 0.2 mL CH_2Cl_2) over 6 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether/triethylamine; 66:34:0.1 (v/v/v), followed by silica; petroleum ether/CH_2Cl_2/triethylamine; 40:60:0.1 (v/v/v)] providing a green solid with a metallic luster (11.7 mg, 26%). Data are in full accordance with the above mentioned protocol.

3-(4-Cyanophenyl)-5-phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6).



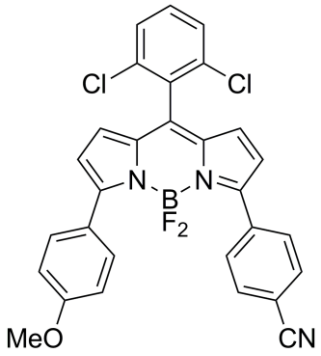
3-PhenylBODIPY **5a** (41.3 mg, 0.1 mmol) and 4-cyanobenzenediazonium tetrafluoroborate **4c** (32.6 mg, 0.15 mmol) were dissolved in acetone (0.8 mL). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (5.6 mg, 0.03 mmol in 0.2 mL CH_2Cl_2) over 9 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 1:1 (v/v)] providing a purple solid (12.2 mg, 24%). Mp: transition at 228 °C, melting point at 252 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.05 (d, 2H, *J* = 8.50 Hz), 7.96-7.89 (m, 2H), 7.71 (d, 2H, *J* = 8.65 Hz), 7.55-7.42 (m, 6H), 6.76 (d, 1H, *J* = 4.30 Hz), 6.69 (d, 1H, *J* = 4.35 Hz), 6.66 (d, 1H, *J* = 4.15 Hz), 6.60 (d, 1H, *J* = 4.15 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 162.4, 155.4, 138.1, 137.1, 137.0, 136.0, 135.7, 132.1, 131.9, 131.8, 131.4, 131.0, 130.6, 130.1, 130.1, 130.0, 129.8, 129.7, 129.7, 128.6, 128.4, 128.3, 122.9, 120.7, 118.9, 112.7 ppm; MS (EI, *m/z*): 513 (100%), 514 (47%), 515 (68%); HRMS (*m/z*): calculated for $C_{28}H_{16}BCl_2F_2N_3$ 513.07824, measured 513.0792.

3-(4-Cyanophenyl)-5-phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6).



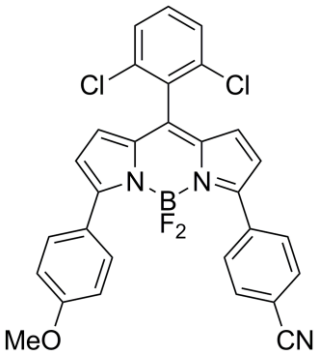
3-(4-Cyanophenyl)-BODIPY **5c** (43.8 mg, 0.1 mmol) and benzenediazonium tetrafluoroborate **4a** (28.8 mg, 0.15 mmol) were dissolved in acetone (0.8 mL). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (5.6 mg, 0.03 mmol in 0.2 mL CH_2Cl_2) over 9 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 4:6 (v/v), followed by silica; petroleum ether/ethyl acetate; 3:1 (v/v)] providing a purple solid (37.6 mg, 73%). Data are in full accordance with the above mentioned protocol.

3-(4-Cyanophenyl)-5-(4-methoxyphenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (7).



3-(4-Cyanophenyl)-BODIPY **5c** (43.8 mg, 0.1 mmol) and 4-methoxybenzenediazonium tetrafluoroborate **4g** (33.3 mg, 0.15 mmol) were dissolved in acetone (0.8 mL). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (5.6 mg, 0.03 mmol in 0.2 mL CH_2Cl_2) over 9 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography [silica; petroleum ether/diethyl ether; 2:1 (v/v)] providing a blue solid with a green metallic luster (29.6 mg, 54%). Mp 295 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.01 (d, 2H, *J* = 8.45 Hz), 7.96 (d, 2H, *J* = 8.85 Hz), 7.71 (d, 2H, *J* = 8.65 Hz), 7.55-7.40 (m, 3H), 6.99 (d, 2H, *J* = 9.05 Hz), 6.77-6.69 (m, 2H), 6.62-6.55 (m, 2H), 3.88 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 162.8, 161.9, 154.0, 137.5, 137.4, 136.7, 135.8, 135.6, 132.1, 131.9, 131.9, 131.8, 131.7, 131.3, 131.2, 130.1, 130.1, 130.0, 128.4, 127.1, 124.1, 123.1, 120.2, 119.0, 114.2, 112.4, 55.5 ppm; MS (EI, *m/z*): 543 (100%), 455 (47%), 545 (69%); HRMS (*m/z*): calculated for $C_{29}H_{18}BCl_2F_2N_3O$ 543.0888, measured 543.08927.

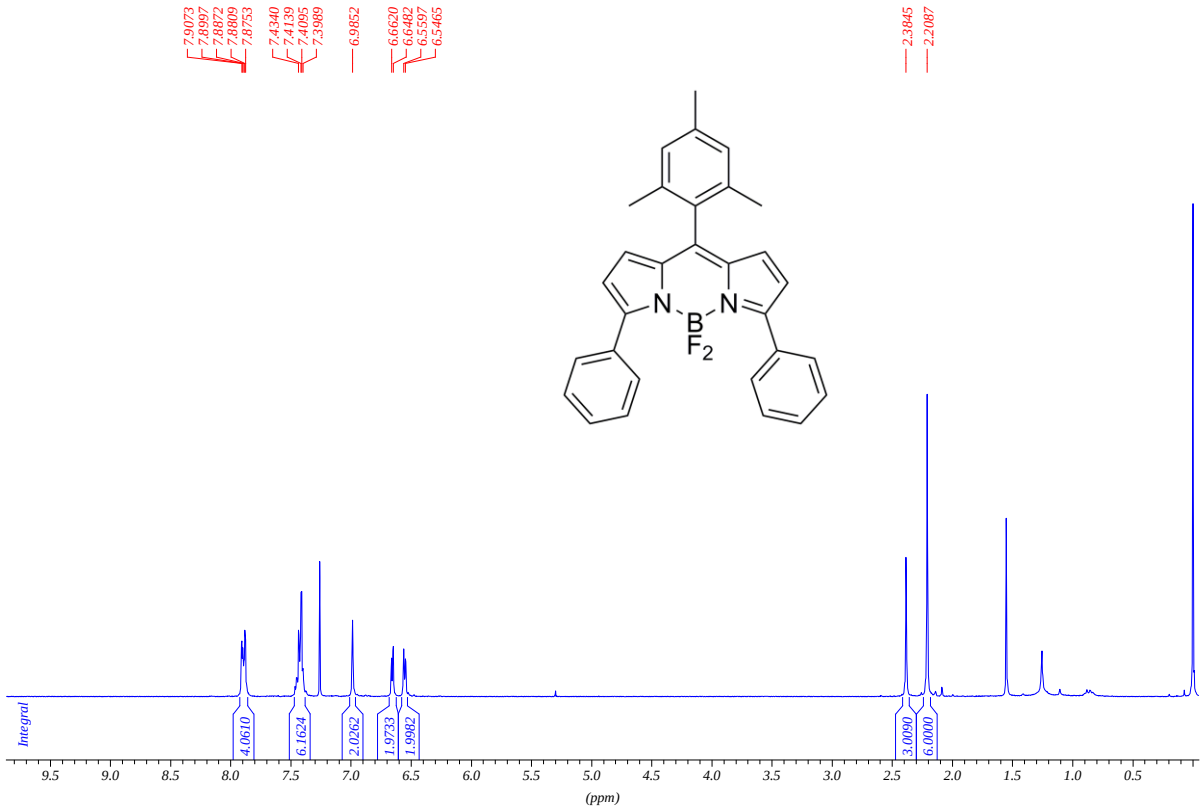
3-(4-Cyanophenyl)-5-(4-methoxyphenyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (7).



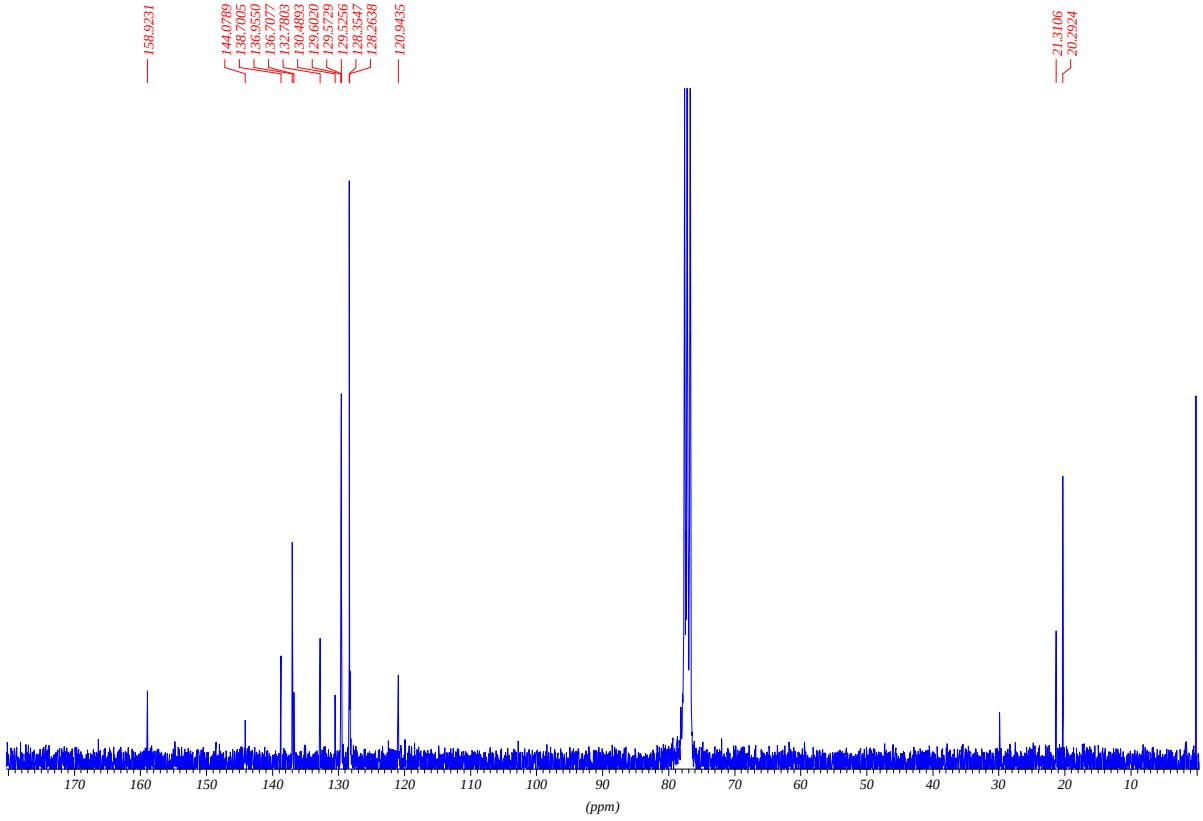
3-(4-Methoxyphenyl)-BODIPY **5g** (44.3 mg, 0.1 mmol) and 4-cyanobenzenediazonium tetrafluoroborate **4c** (32.6 mg, 0.15 mmol) were dissolved in acetone (0.8 mL). To this reaction mixture was added dropwise, at room temperature, a ferrocene solution (5.6 mg, 0.03 mmol in 0.2 mL CH_2Cl_2) over 9 min. After the addition, the reaction mixture was stirred at the same temperature until IR analysis showed complete consumption of the diazonium salt. Next, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography [silica; petroleum ether/CH_2Cl_2; 1:2 (v/v)] providing a blue solid with a green metallic luster (19.3 mg, 36%). Data are in full accordance with the above mentioned protocol.

NMR-spectra of all new compounds

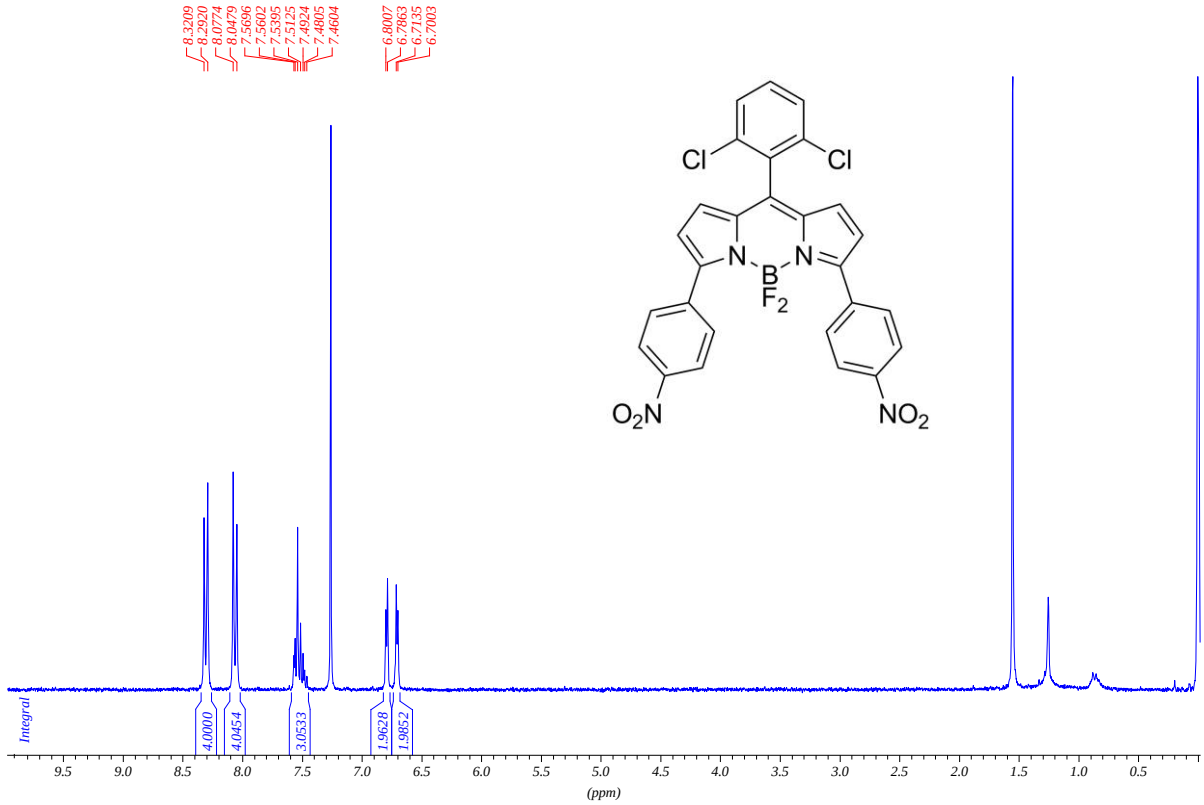
3c, ^{1}H, 300 MHz, $CDCl_3$



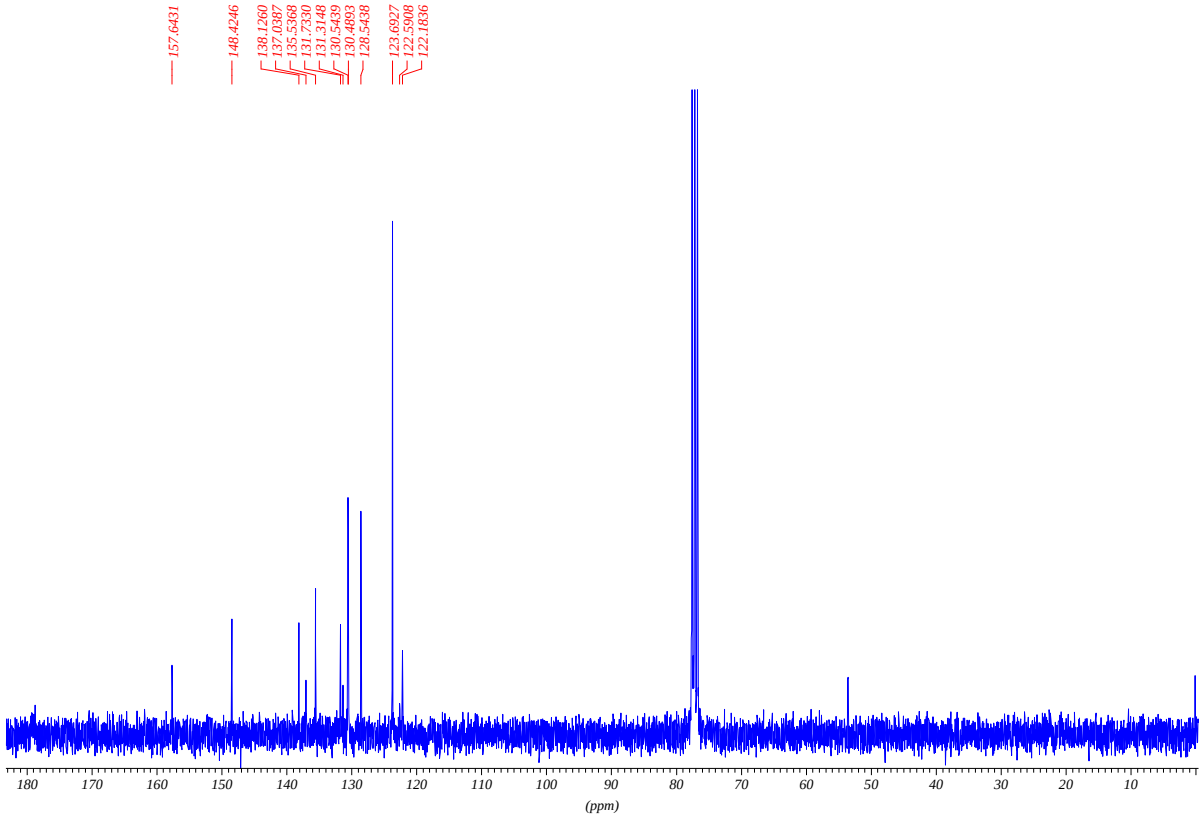
3c, ^{13}C, 75 MHz, $CDCl_3$



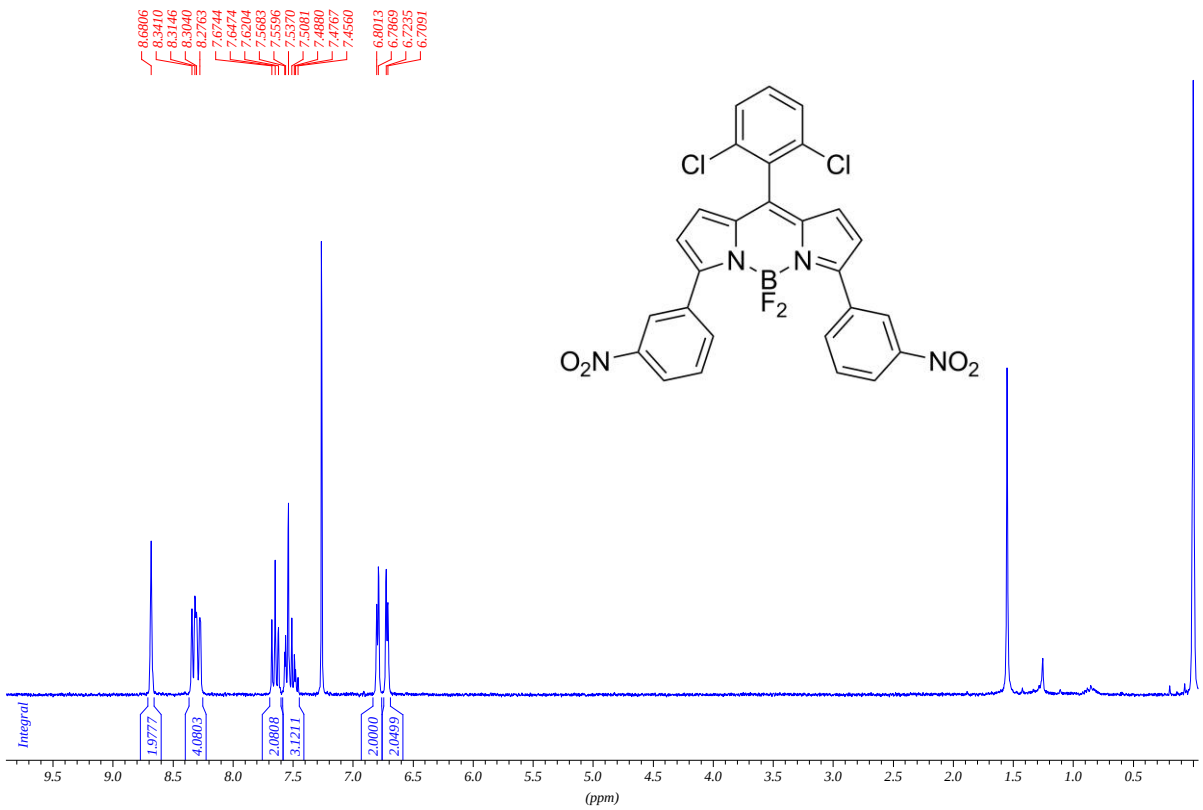
3d, ^{1}H, 300 MHz, $CDCl_3$



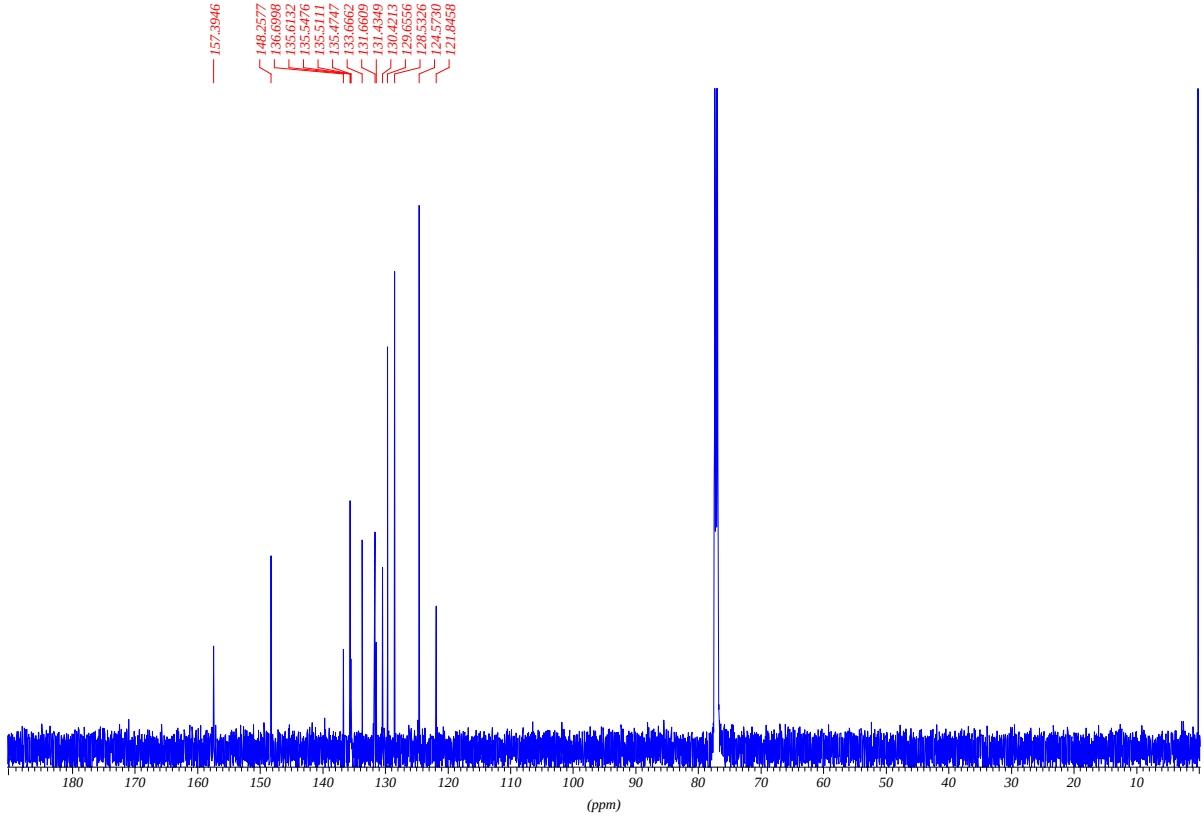
3d, ^{13}C, 75 MHz, $CDCl_3$



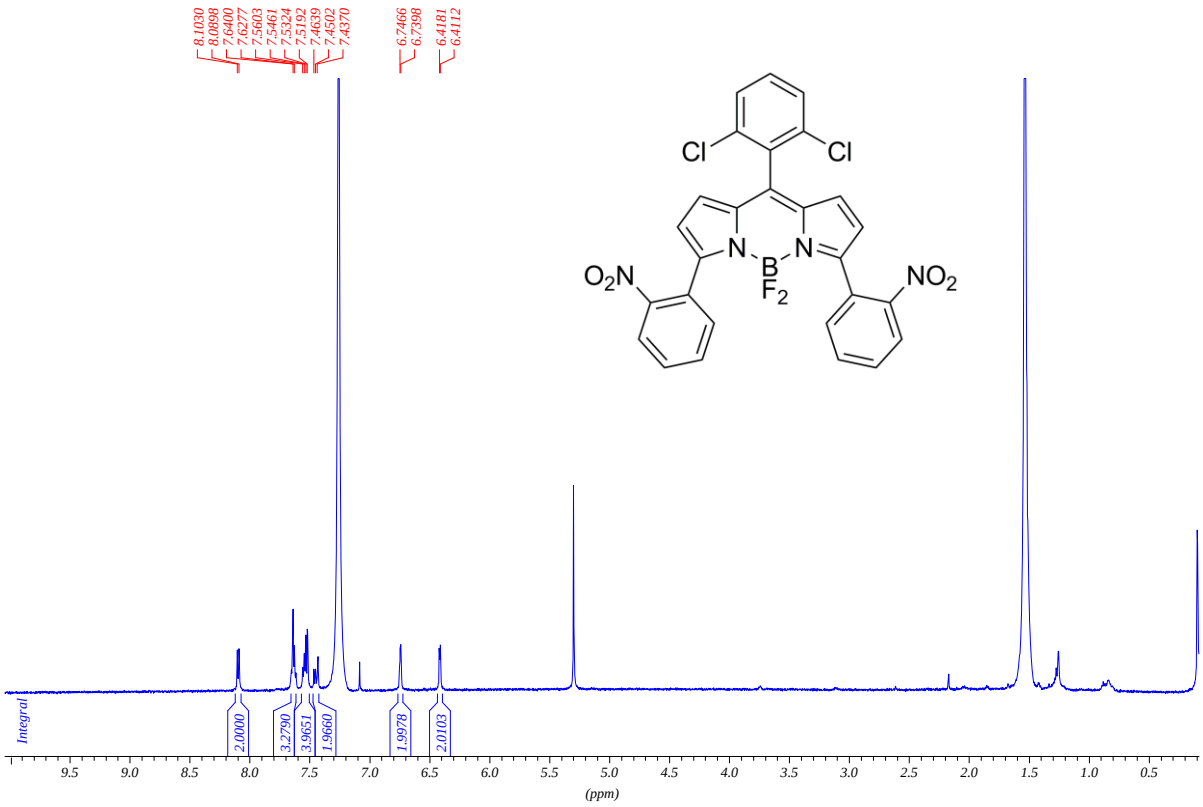
3e, ^{1}H, 300 MHz, $CDCl_3$



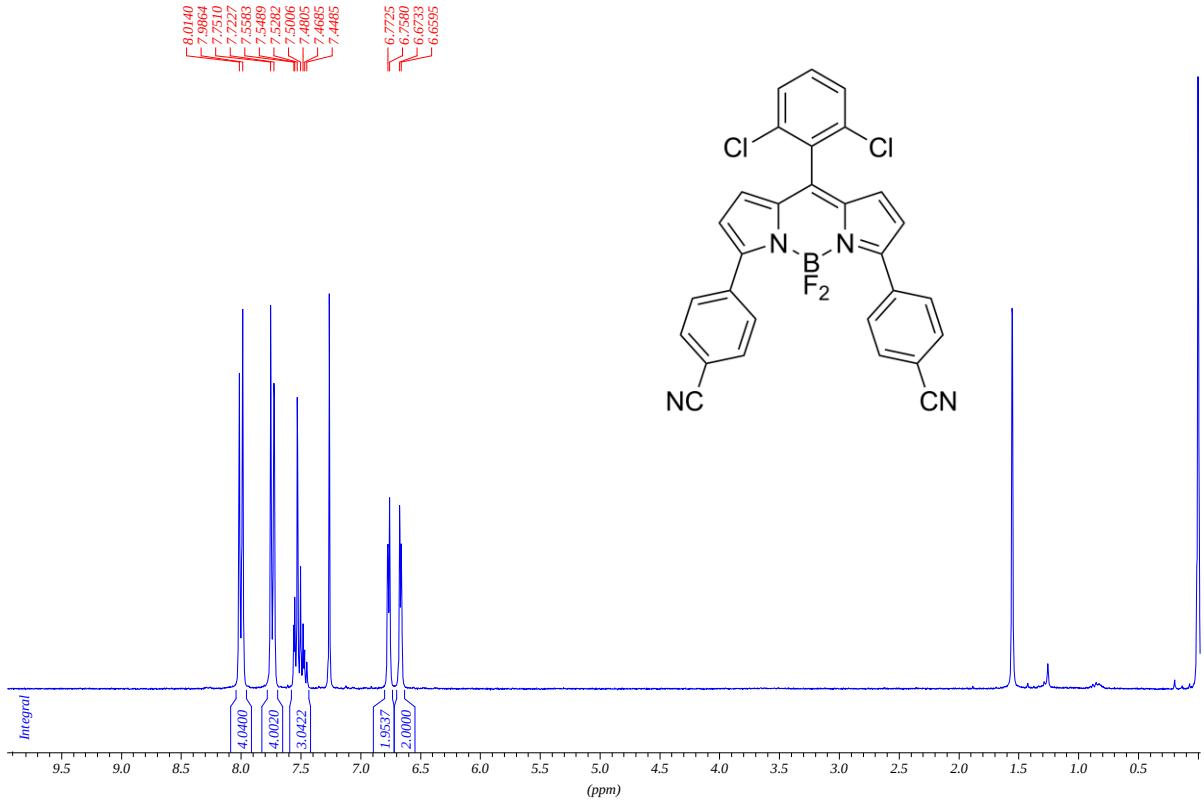
3e, ^{13}C, 150 MHz, $CDCl_3$



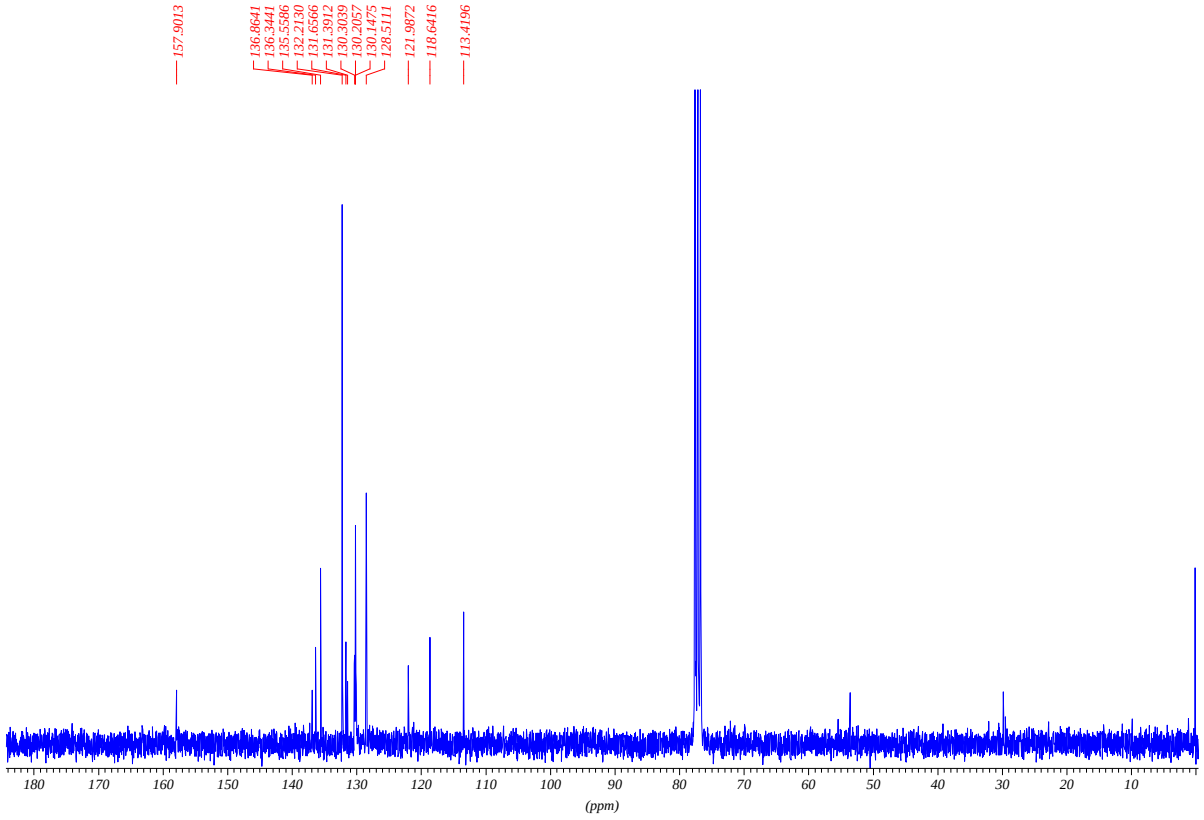
3f, ^{1}H, 600 MHz, $CDCl_3$



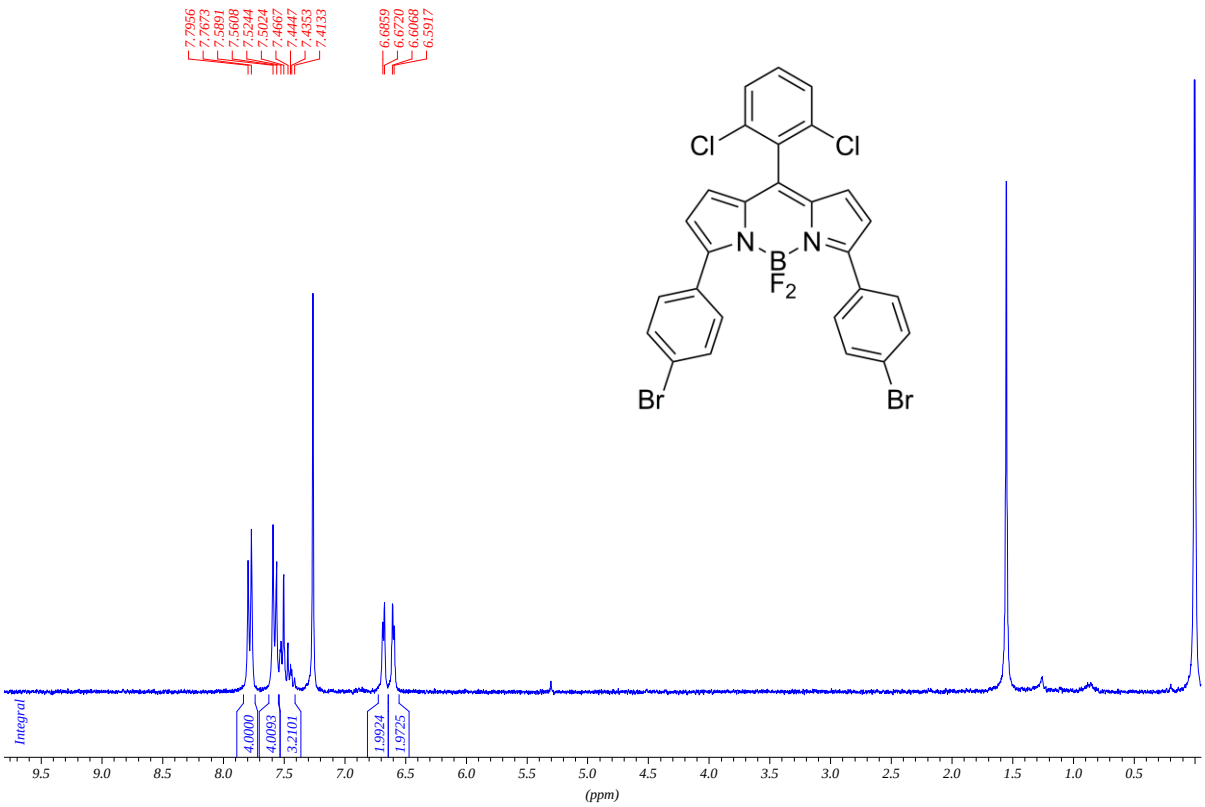
3g, ^{1}H, 300 MHz, $CDCl_3$



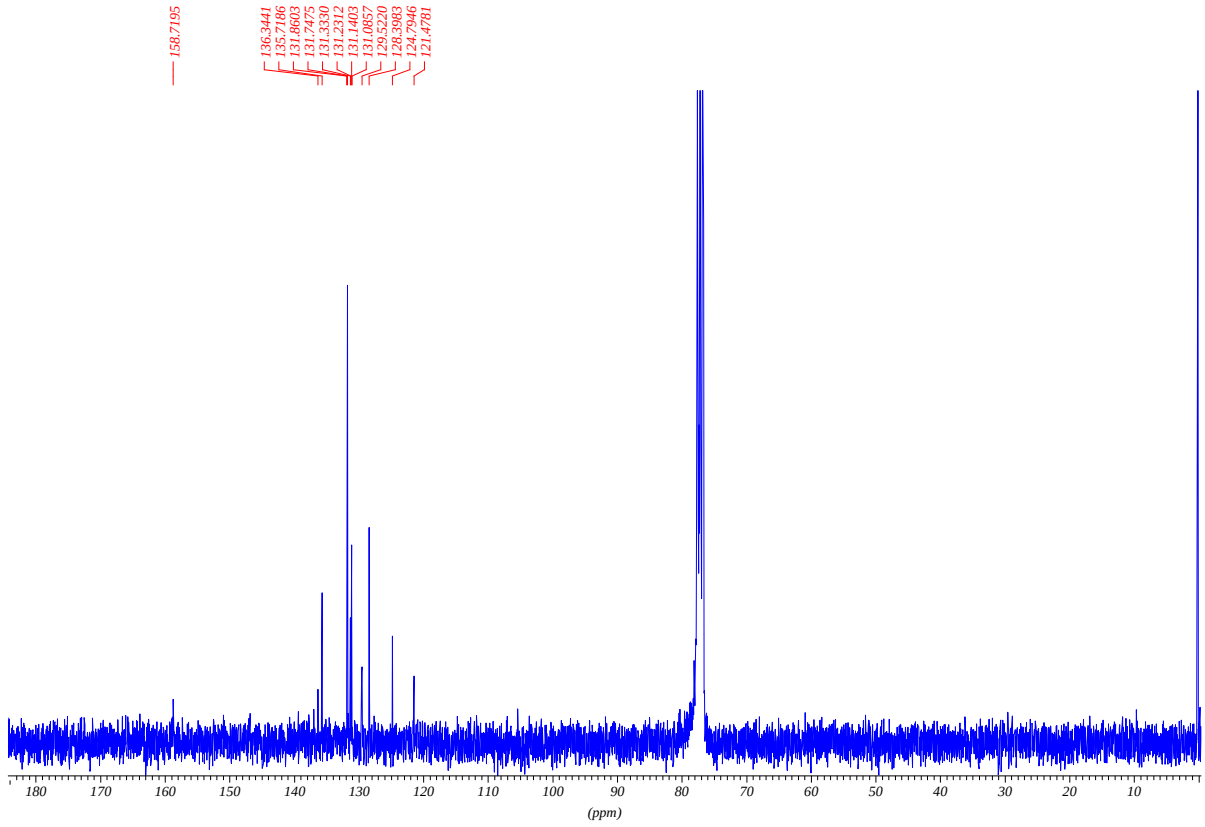
3g, ^{13}C, 75 MHz, $CDCl_3$



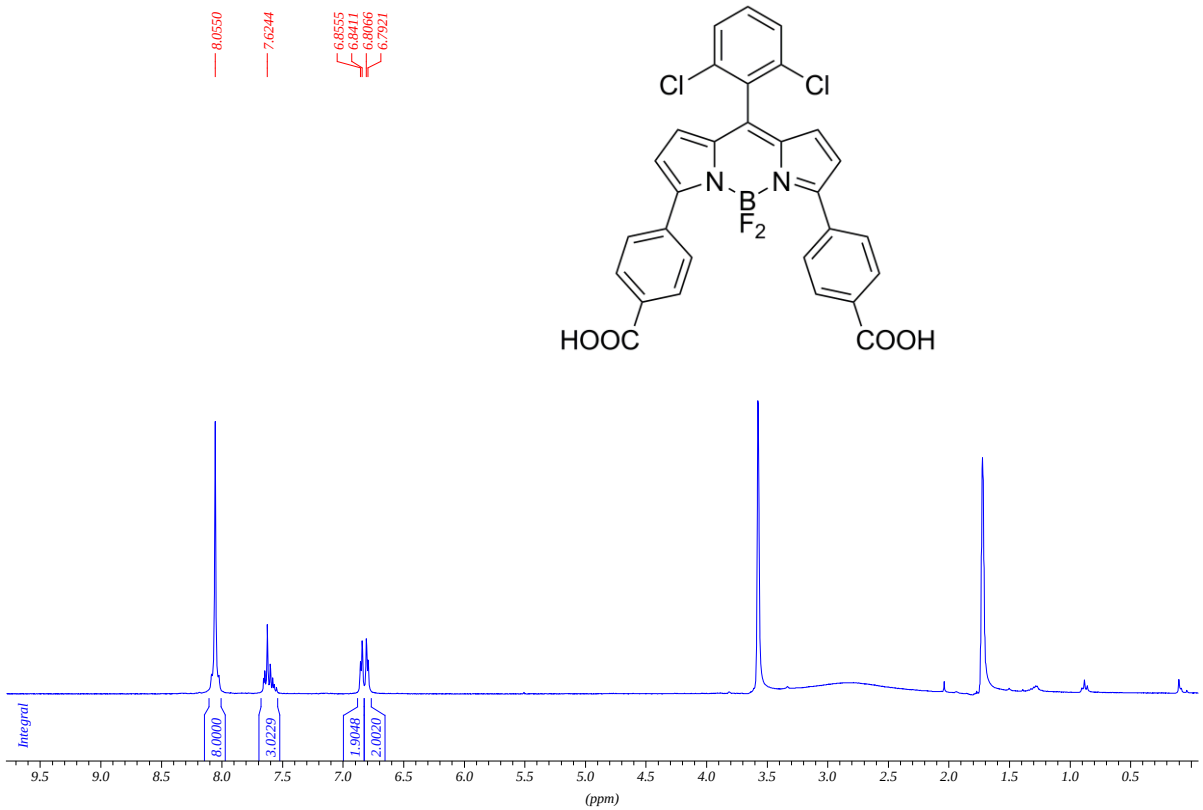
3h, ^{1}H, 300 MHz, $CDCl_3$



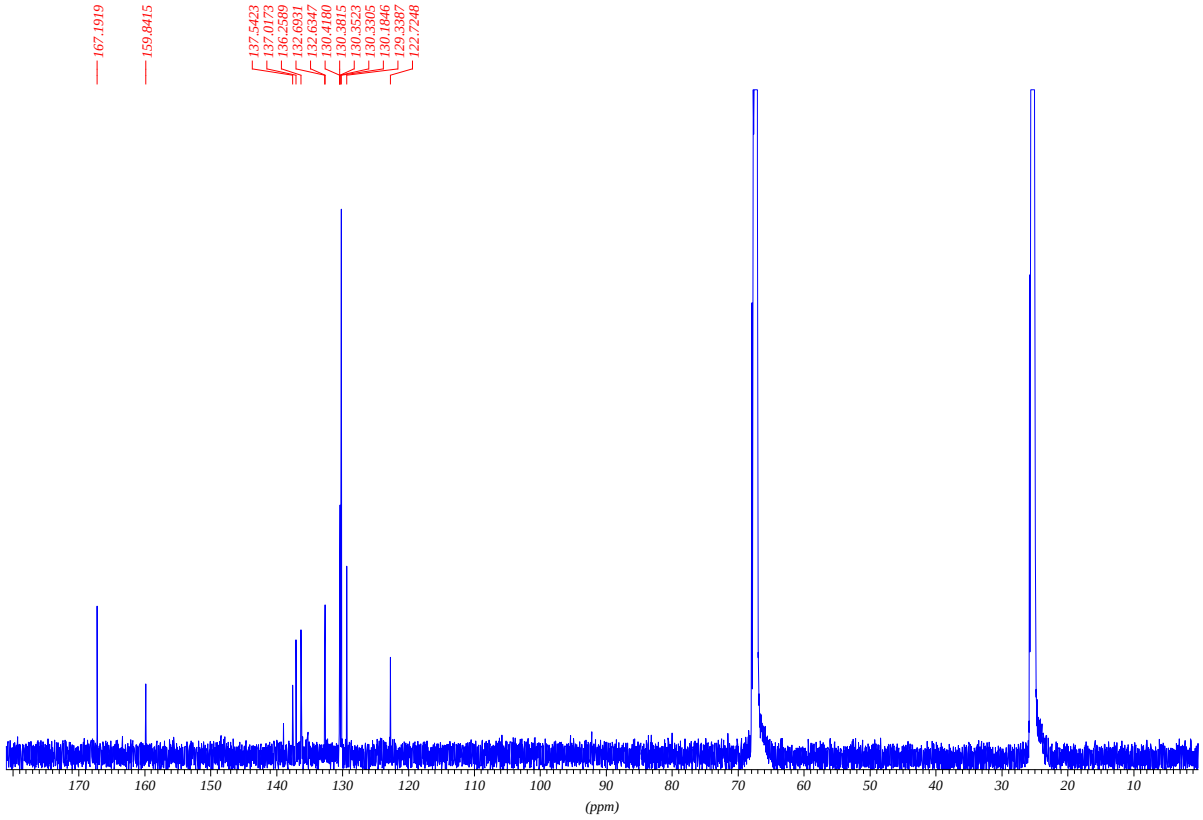
3h, ^{13}C, 75 MHz, $CDCl_3$



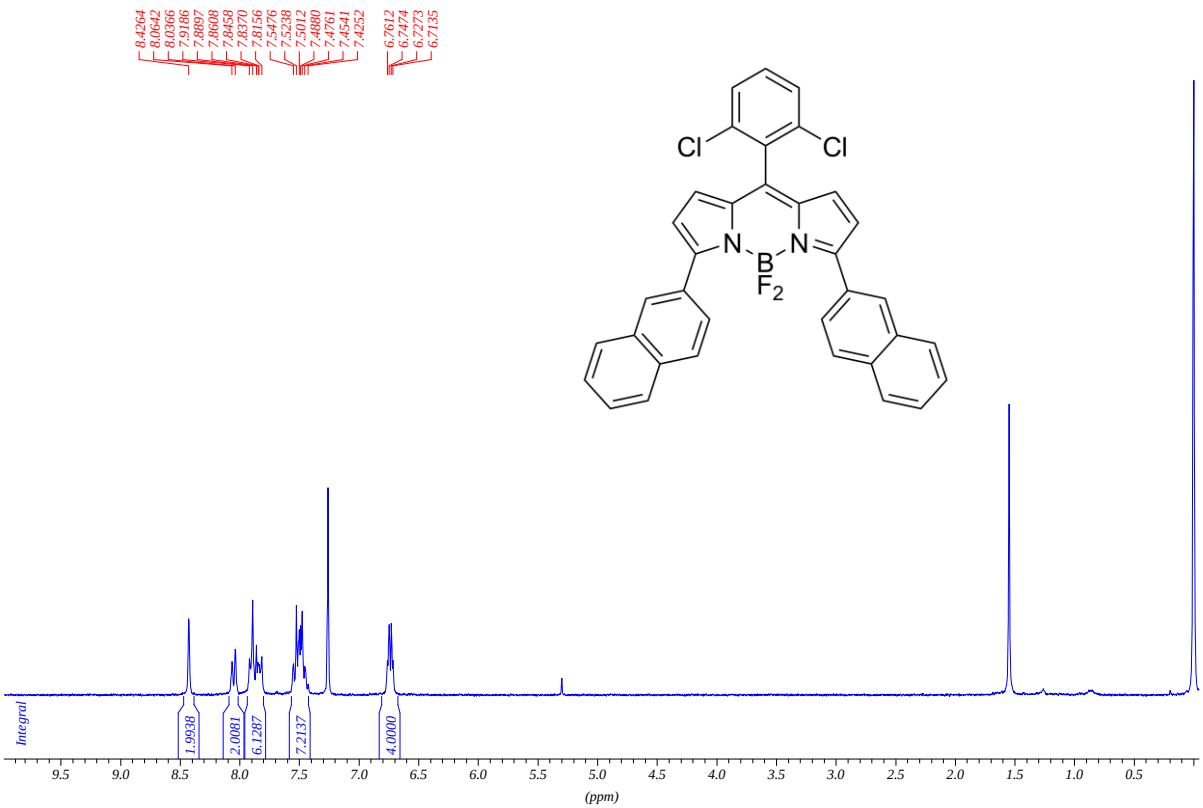
3i, ^{1}H, 300 MHz, THF-d_8



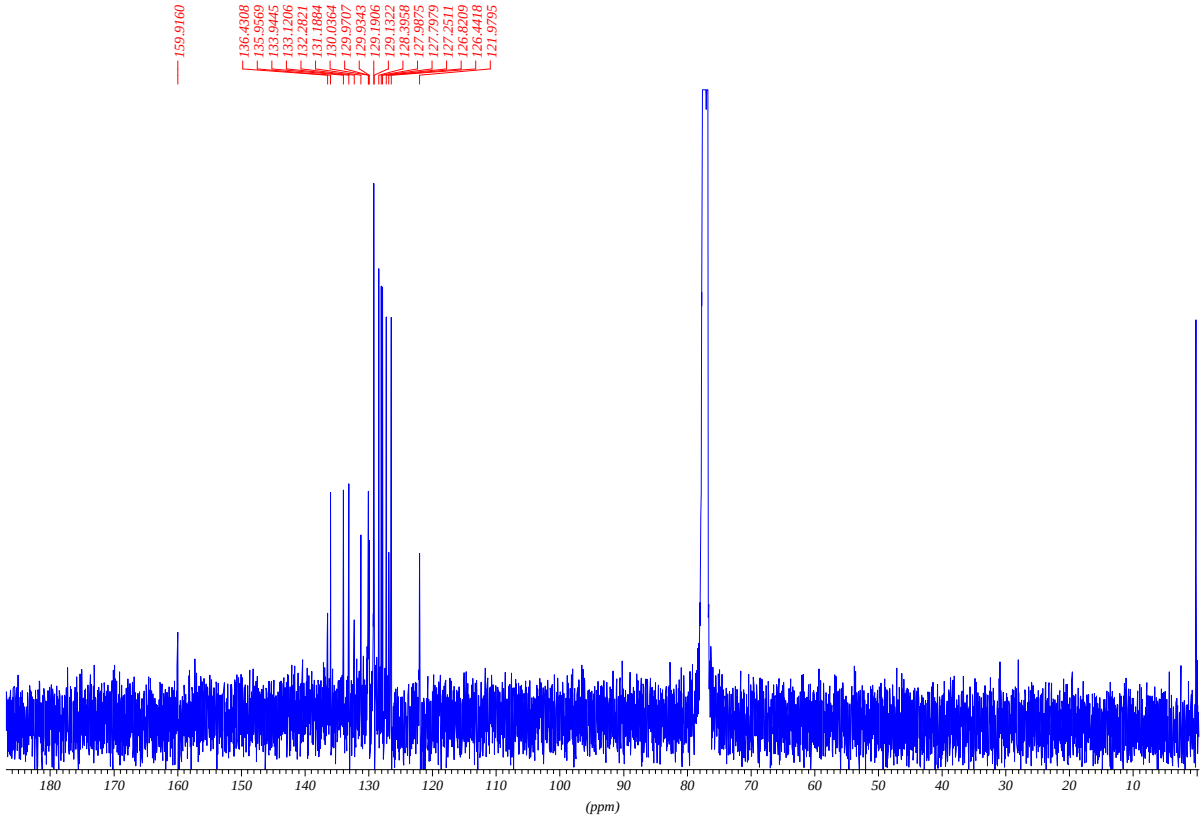
3i, ^{13}C, 150 MHz, THF-d_8



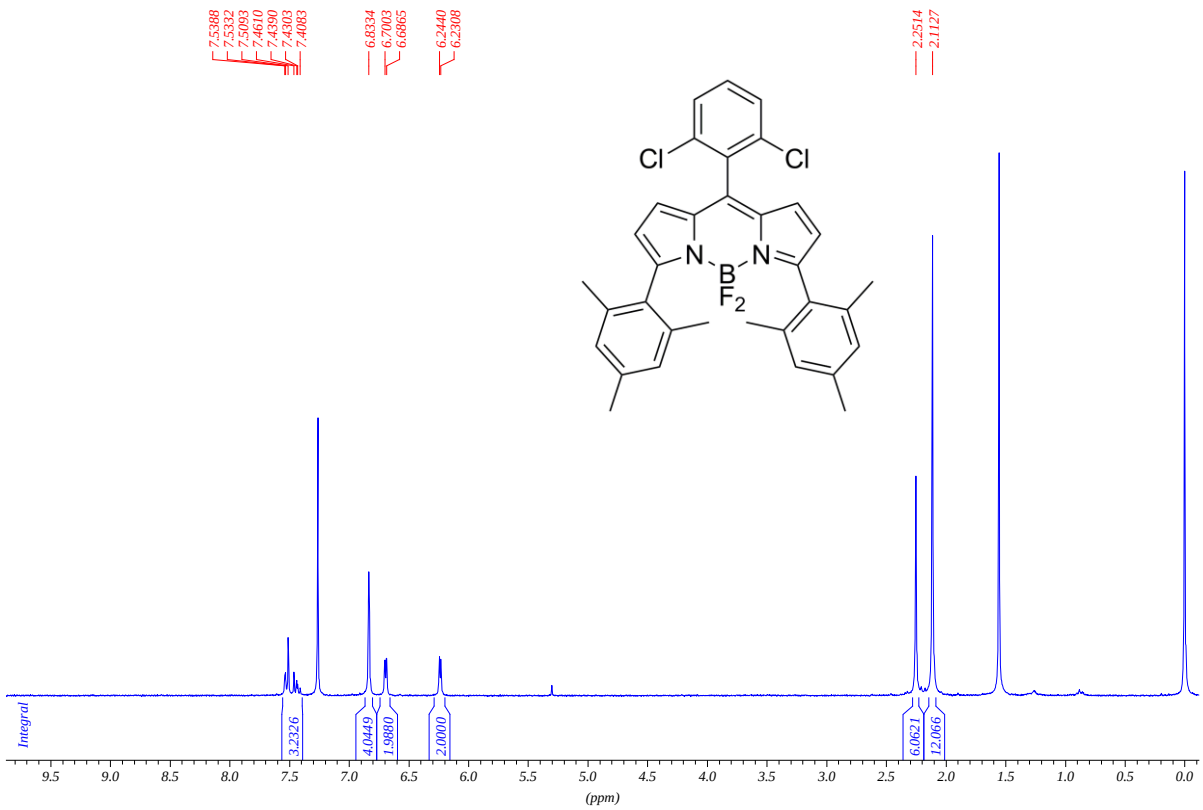
3j, ^{1}H, 300 MHz, $CDCl_3$



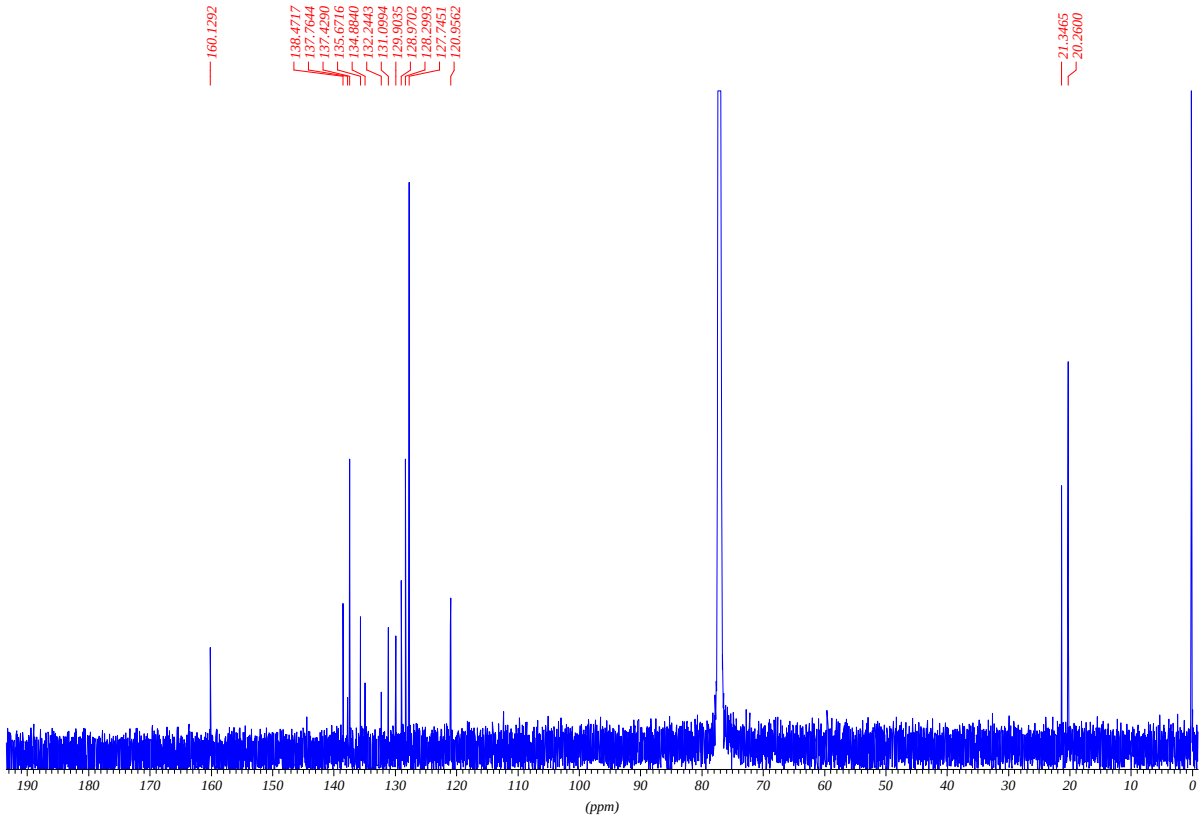
3j, ^{13}C, 100 MHz, $CDCl_3$



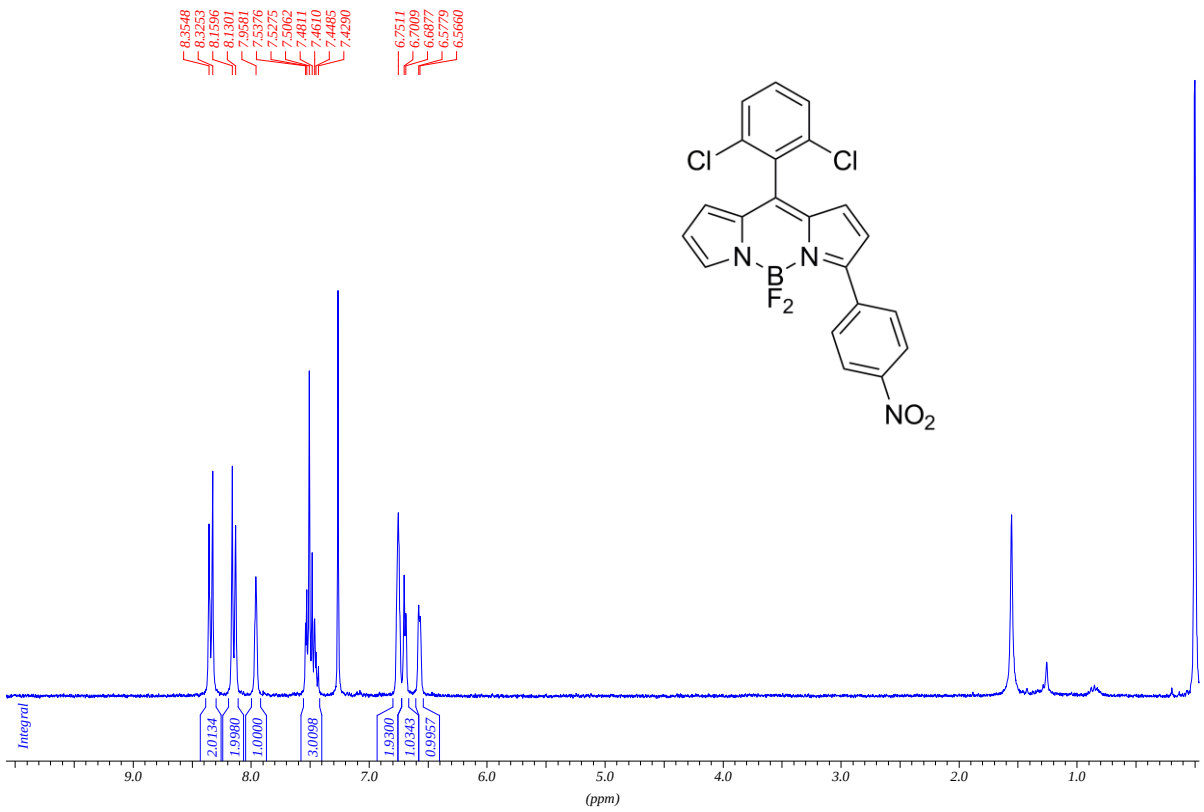
3k, ^{1}H, 300 MHz, $CDCl_3$



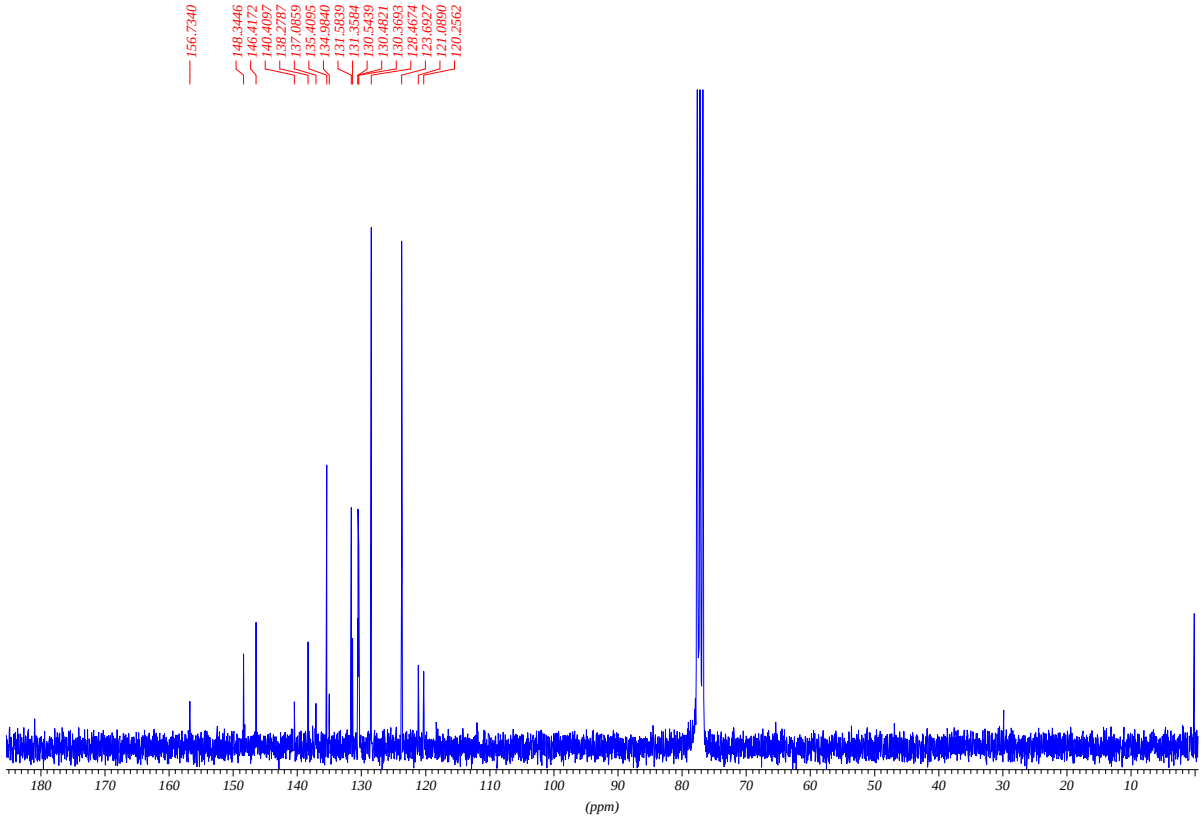
3k, ^{13}C, 150 MHz, $CDCl_3$



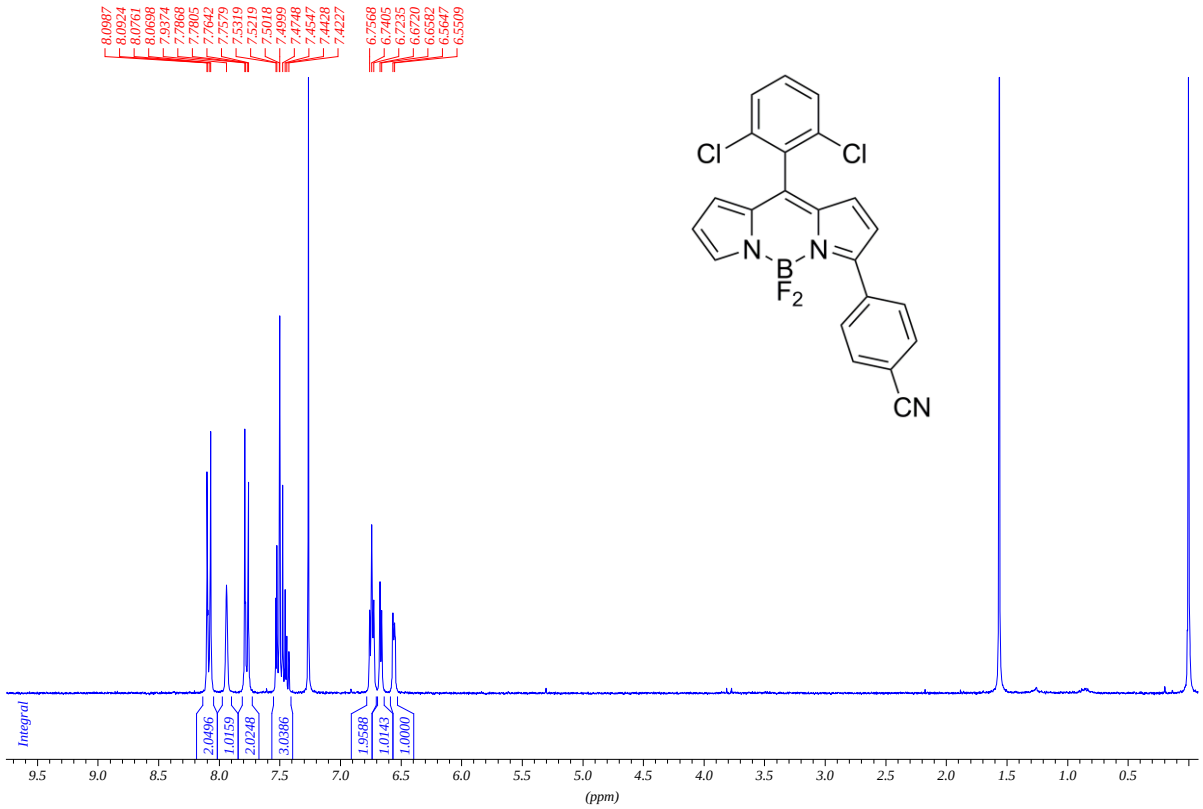
5b, ^{1}H, 300 MHz, $CDCl_3$



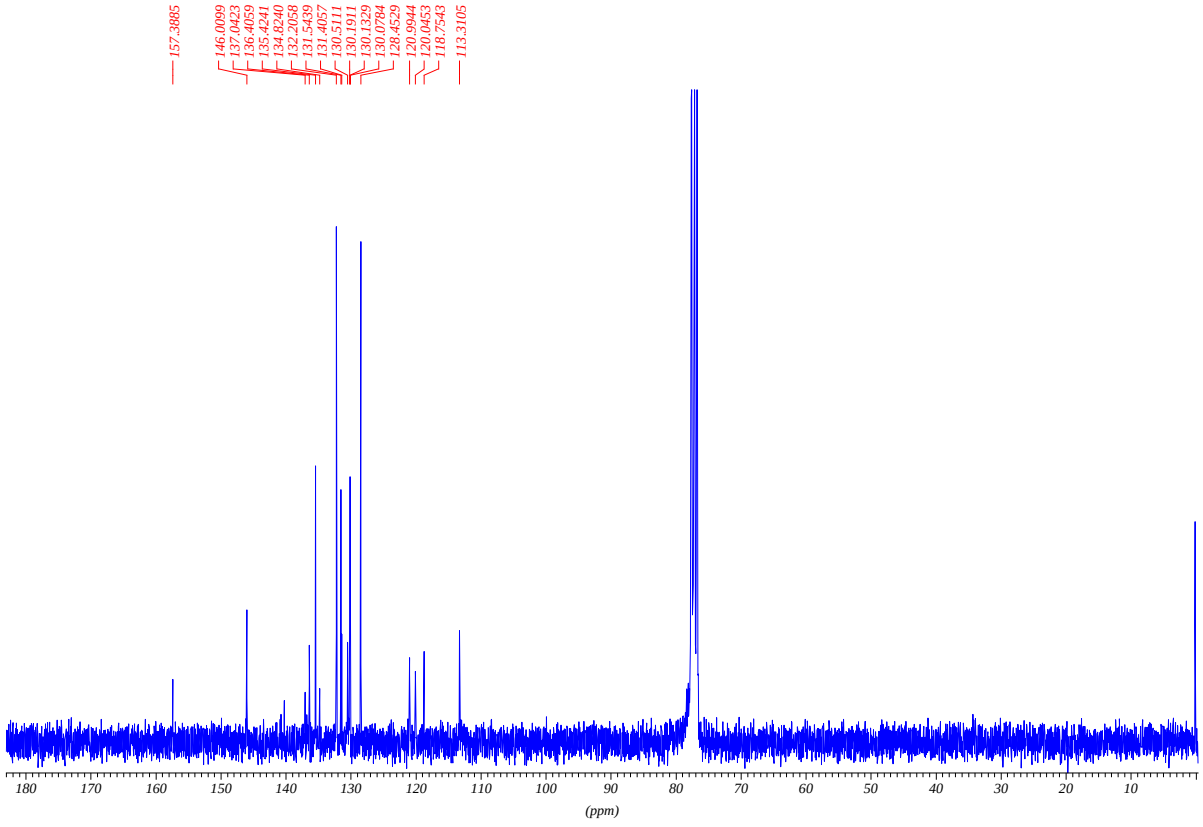
5b, ^{13}C, 75 MHz, $CDCl_3$



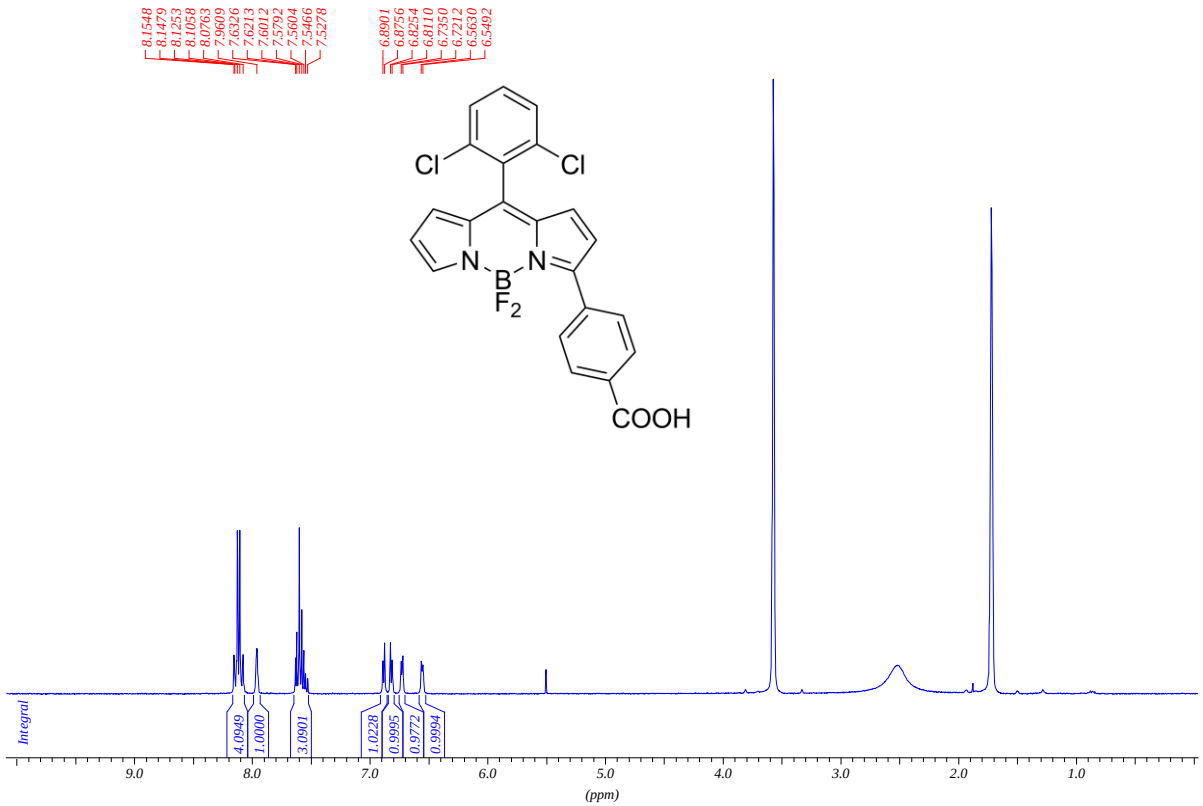
5c, ^{1}H, 300 MHz, $CDCl_3$



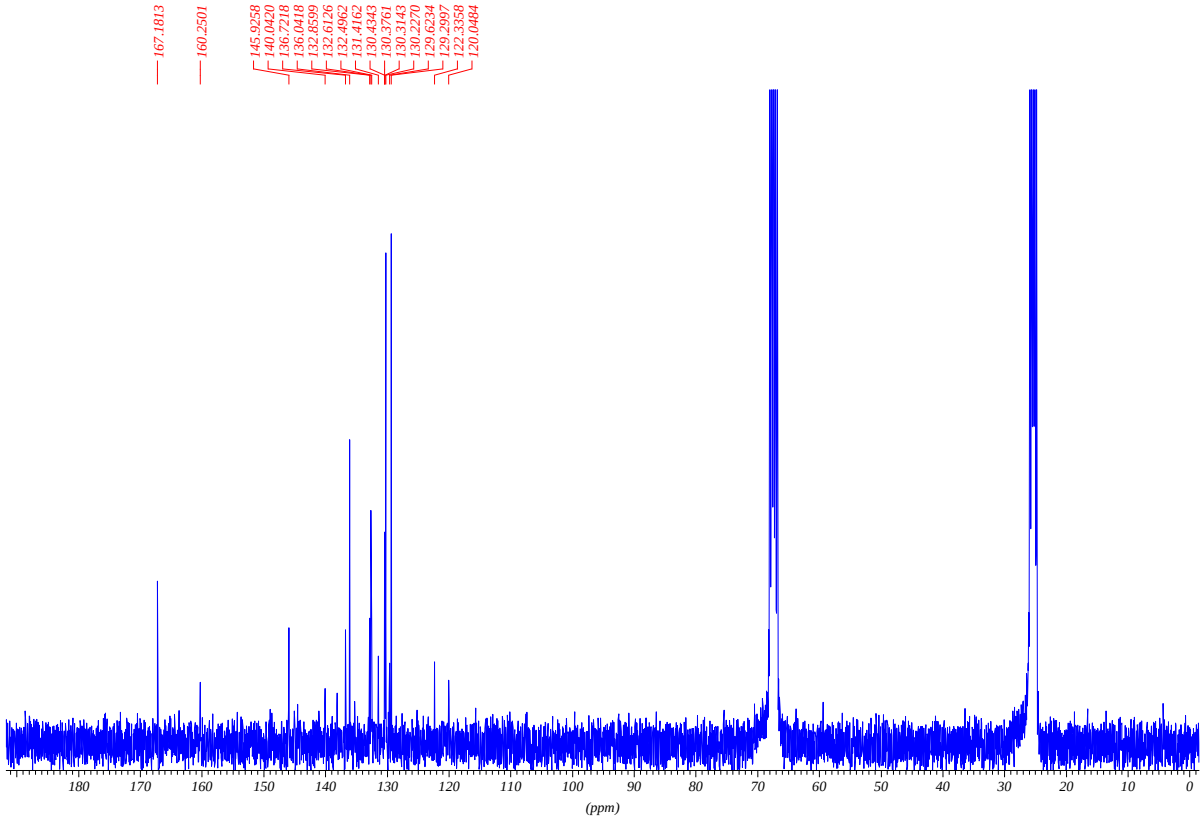
5c, ^{13}C, 75 MHz, $CDCl_3$



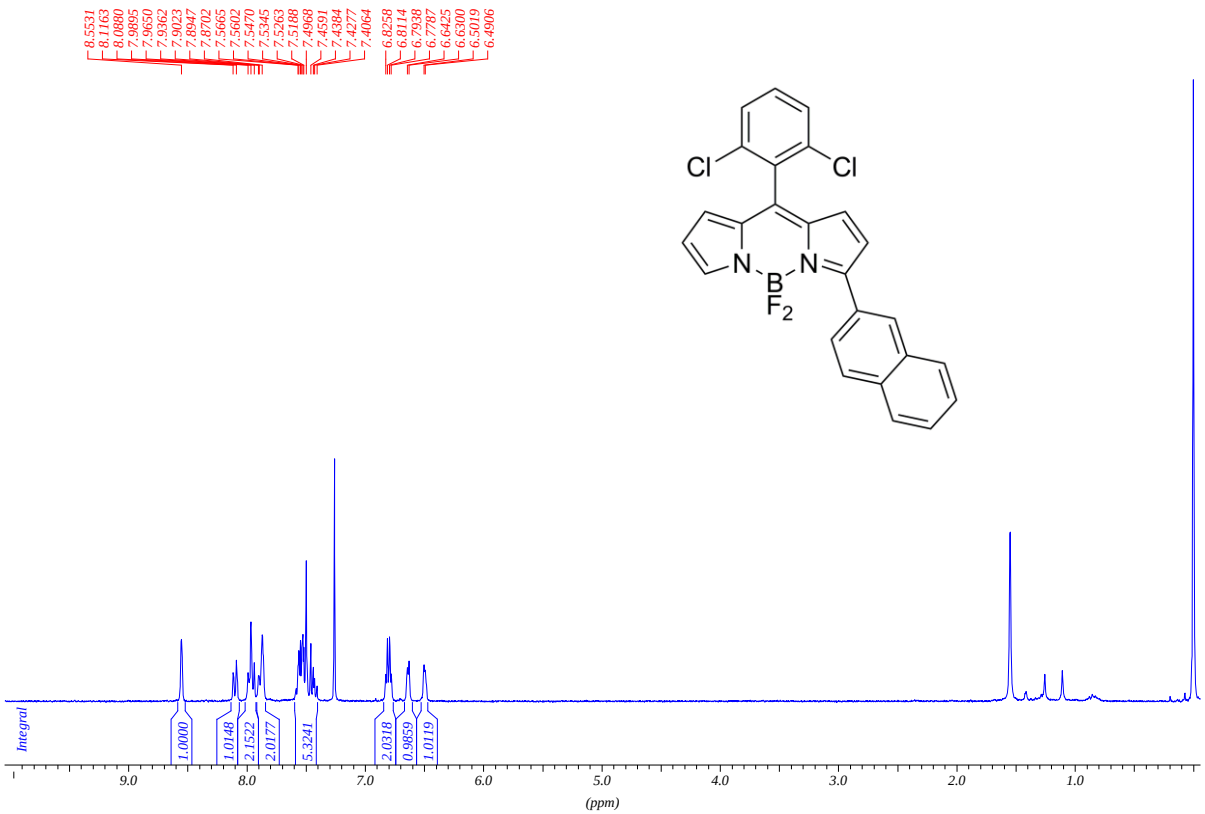
5d, ^{1}H, 300 MHz, THF-d_8



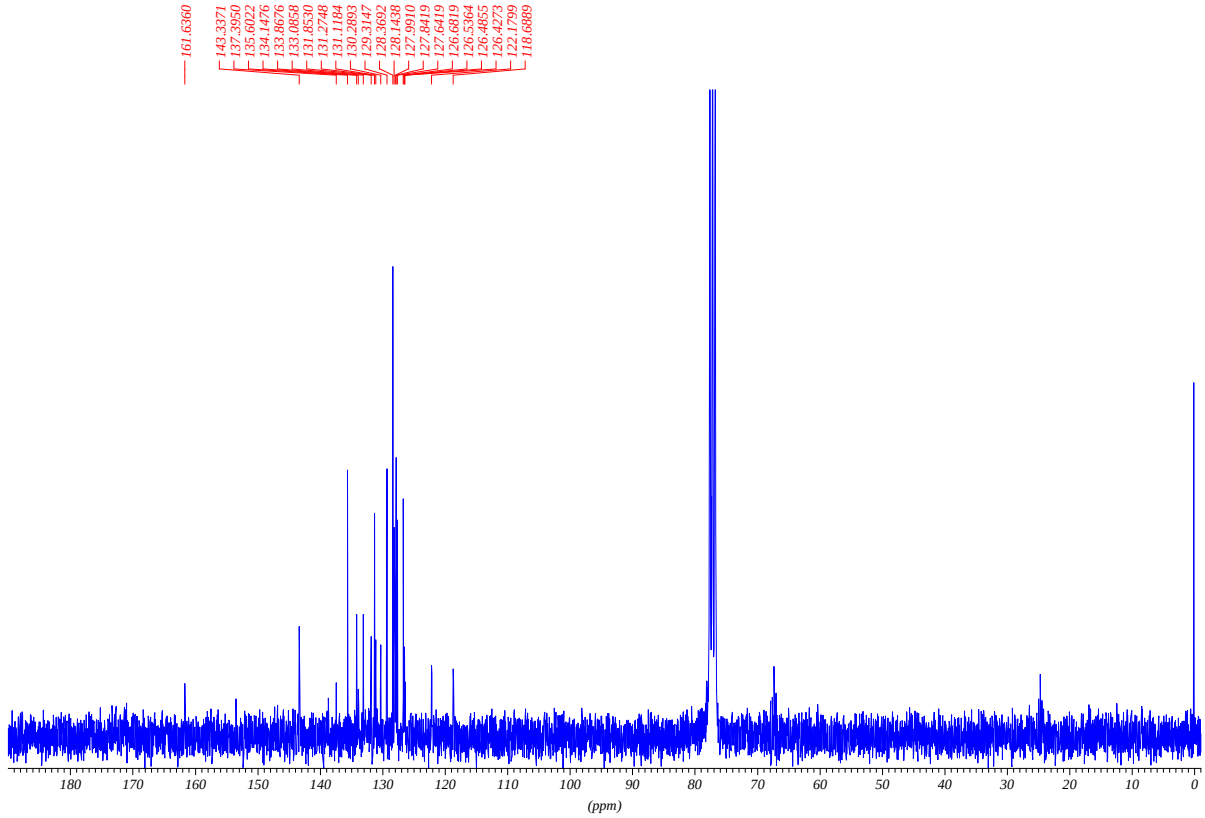
5d, ^{13}C, 75 MHz, THF-d_8



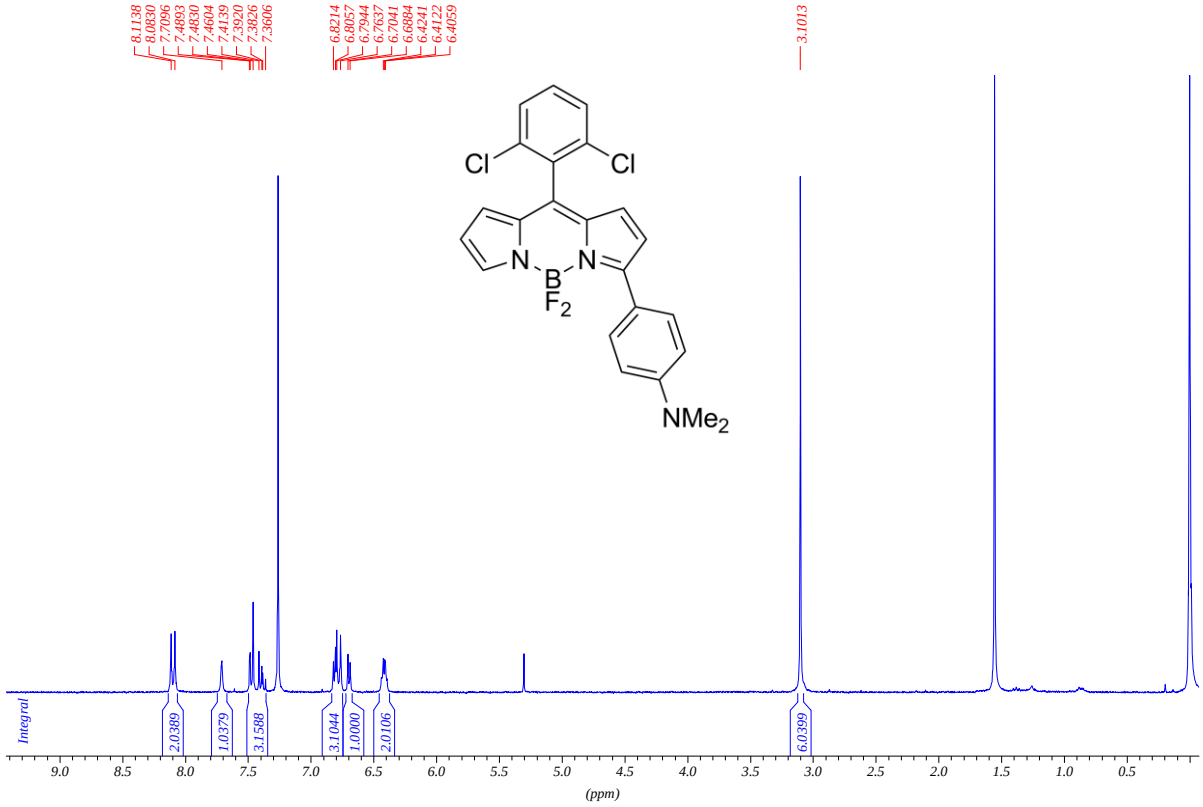
5e, ^{1}H, 300 MHz, $CDCl_3$



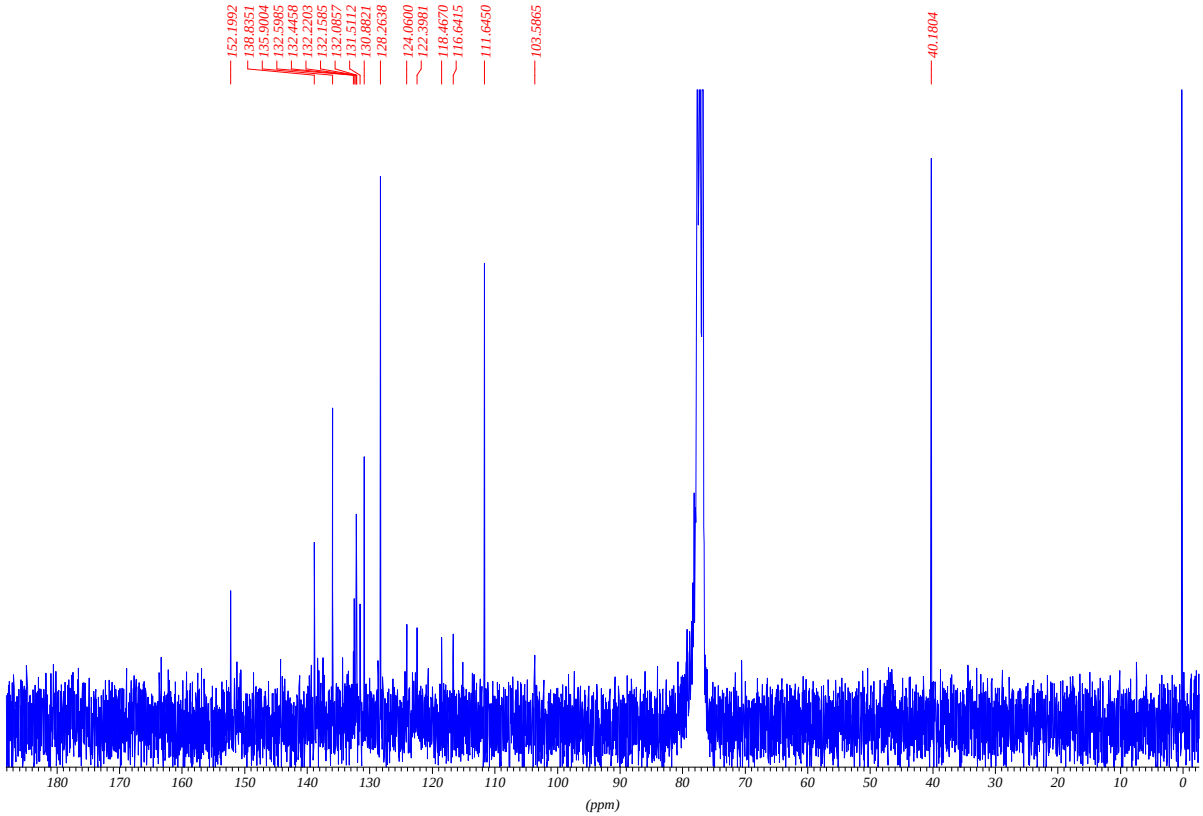
5e, ^{13}C, 75 MHz, $CDCl_3$



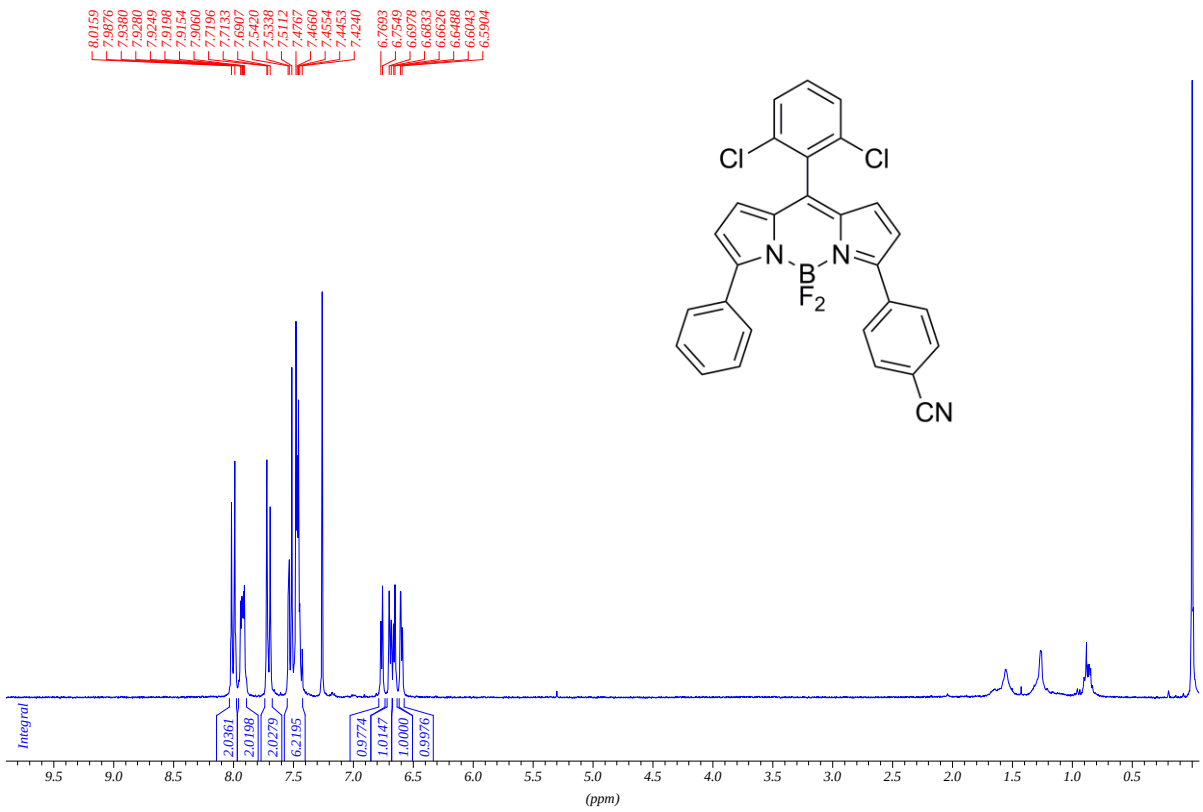
5h, ^{1}H, 300 MHz, $CDCl_3$



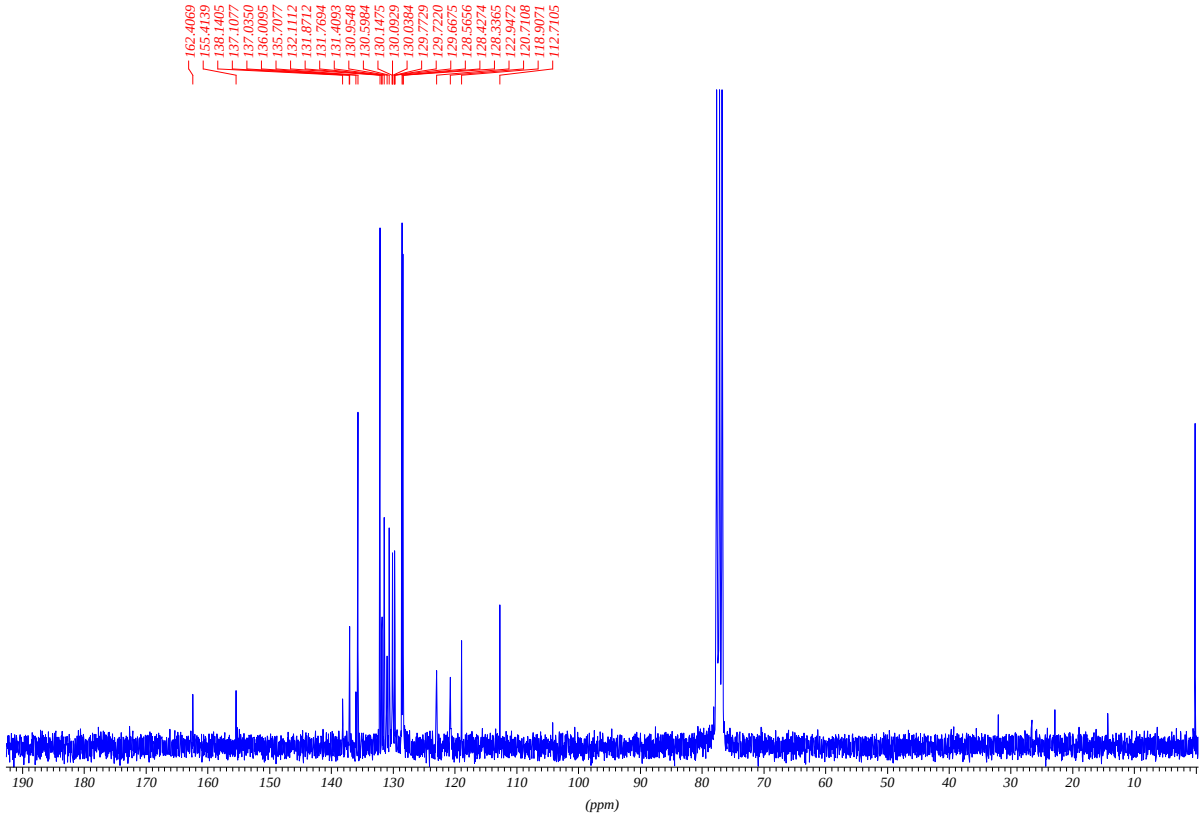
5h, ^{13}C, 75 MHz, $CDCl_3$



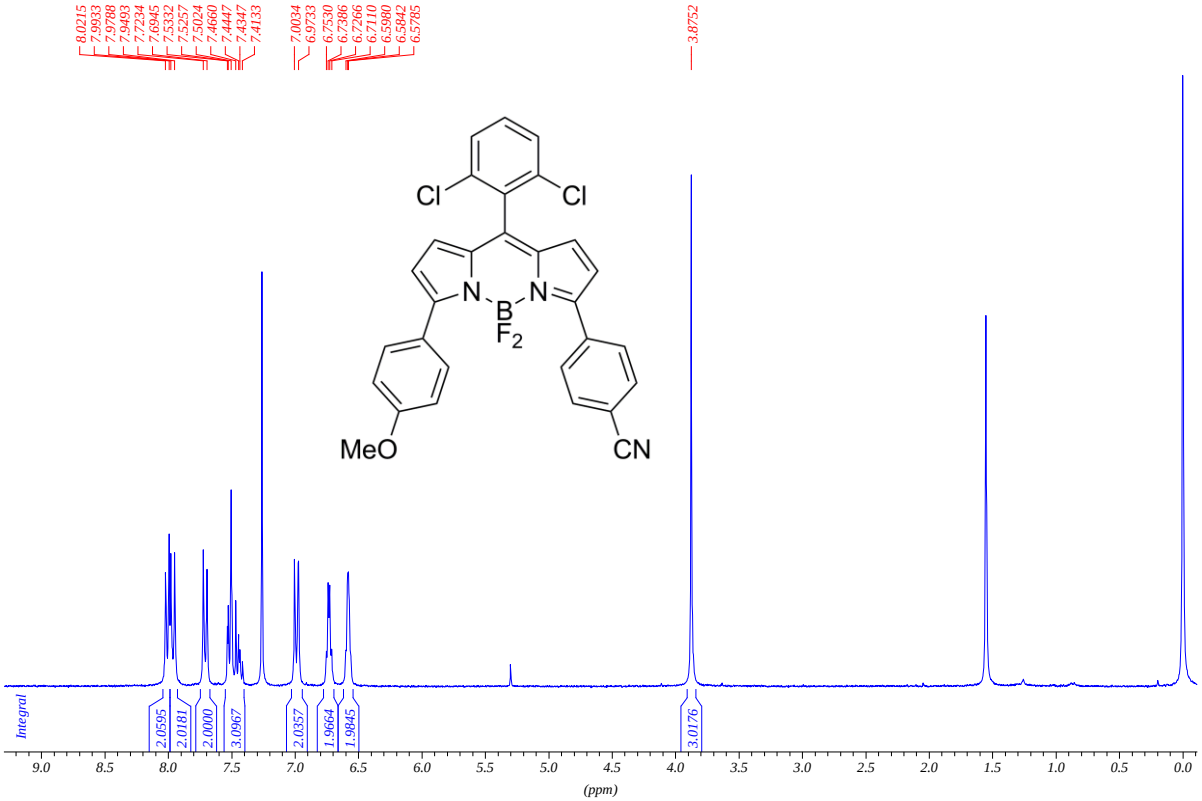
6, ^{1}H, 300 MHz, $CDCl_3$



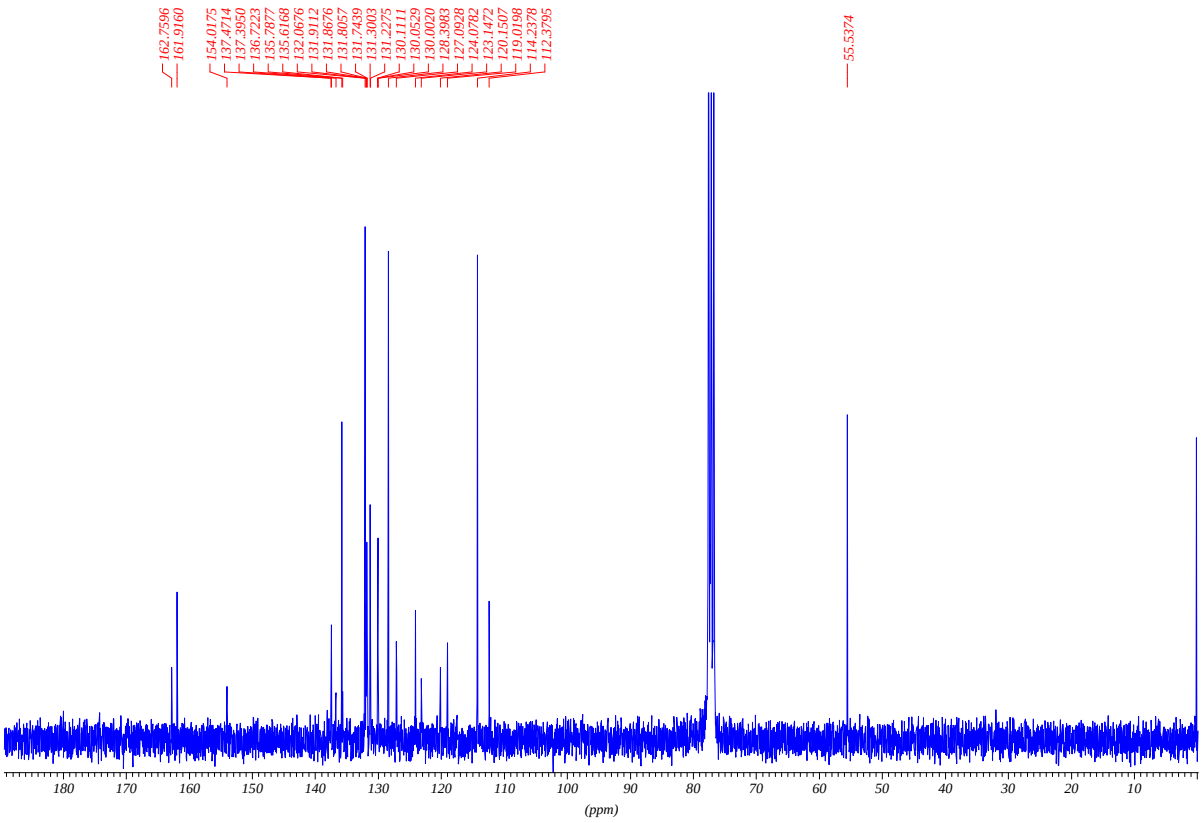
6, ^{13}C, 75 MHz, $CDCl_3$



7, ^{1}H, 300 MHz, $CDCl_3$



7, ^{13}C, 75 MHz, $CDCl_3$



UV–vis spectroscopic data

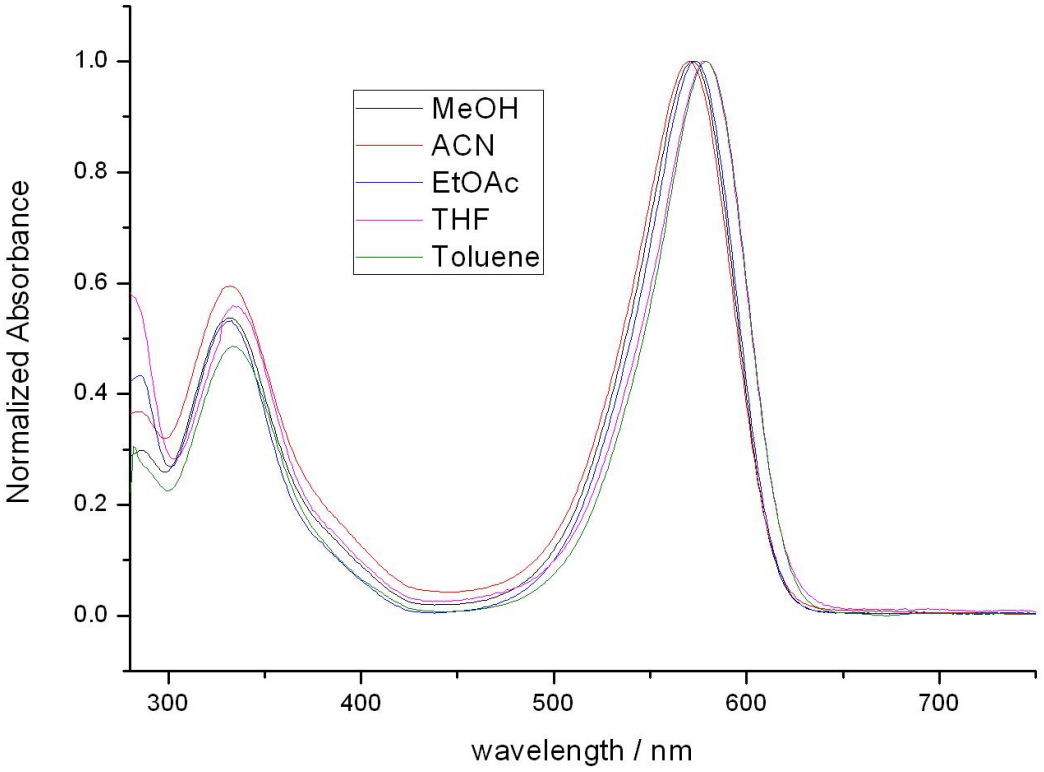


Figure S1a. Normalized UV–vis absorption spectra of 3,5-diarylBODIPY **3d** in the solvents indicated.

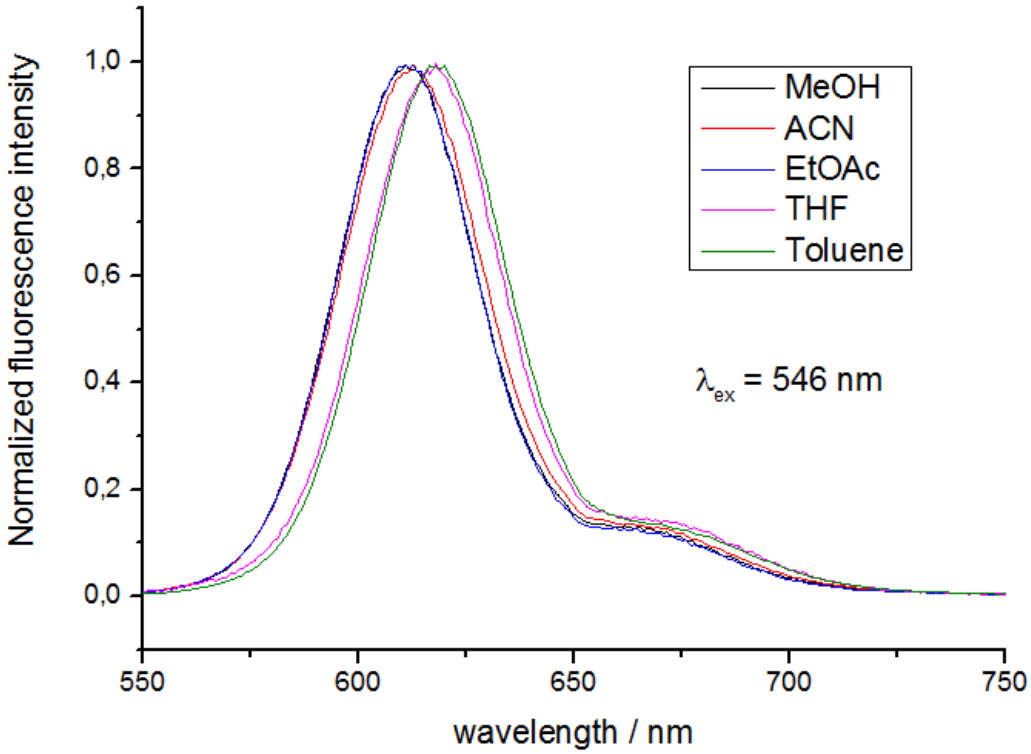


Figure S1b. Corresponding normalized, visible emission spectra of **3d** in the solvents indicated upon excitation at 546 nm.

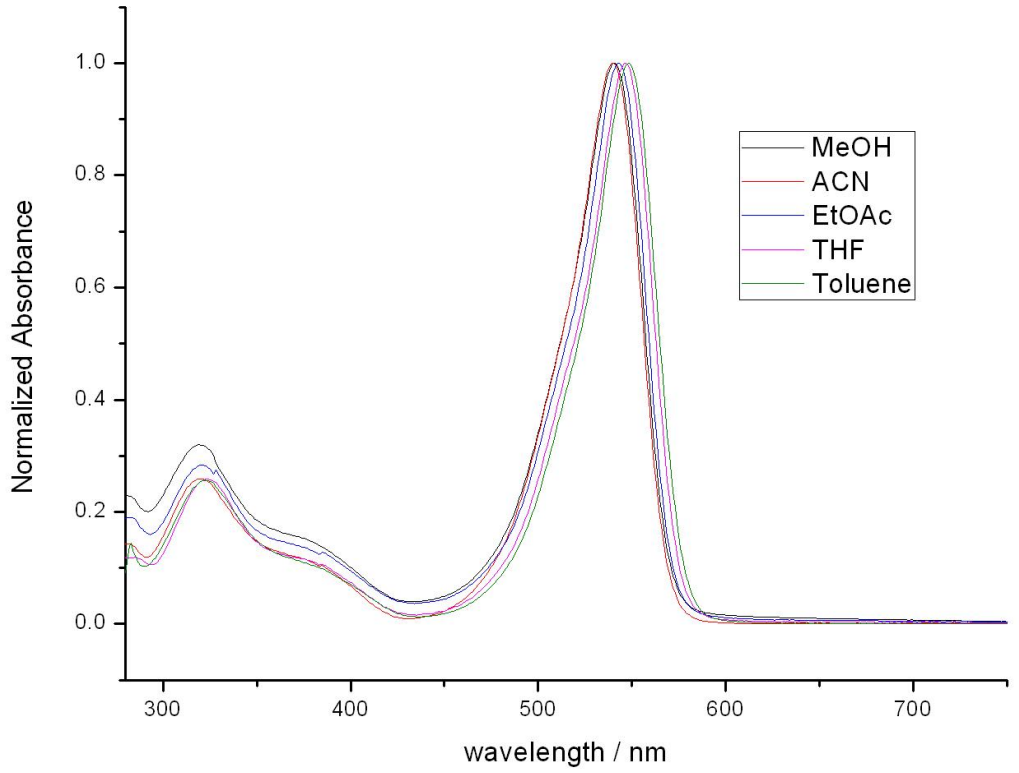


Figure S2a. Normalized UV–vis absorption spectra of 3-arylBODIPY **5b** in the solvents indicated.

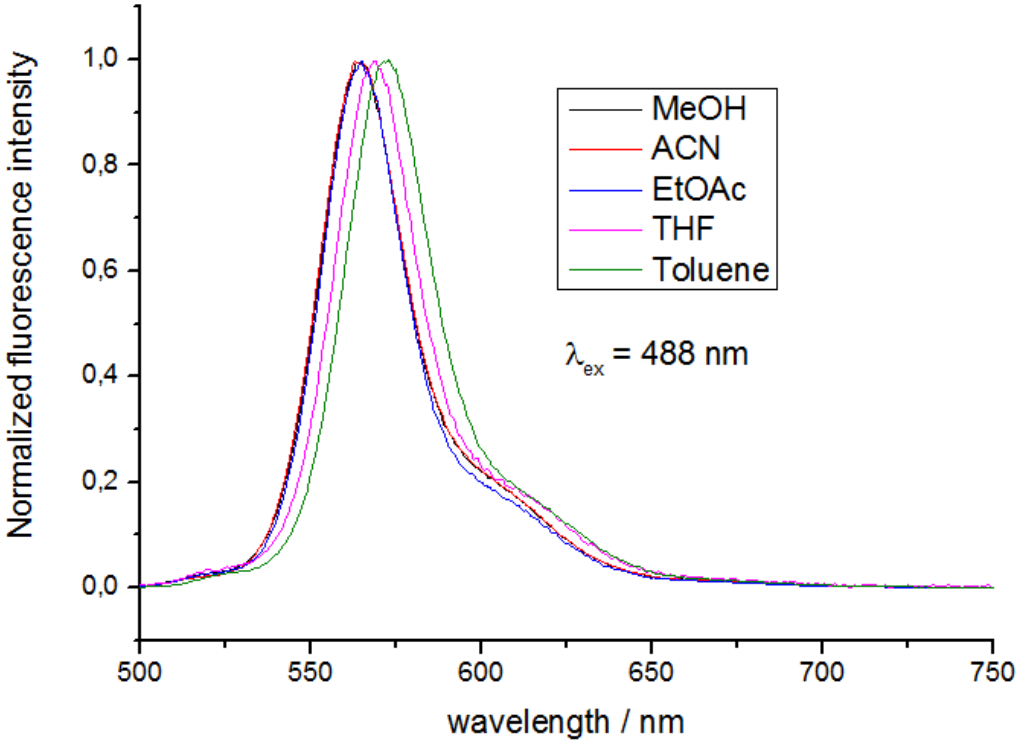


Figure S2b. Corresponding normalized, visible emission spectra of **5b** in the solvents indicated upon excitation at 488 nm.

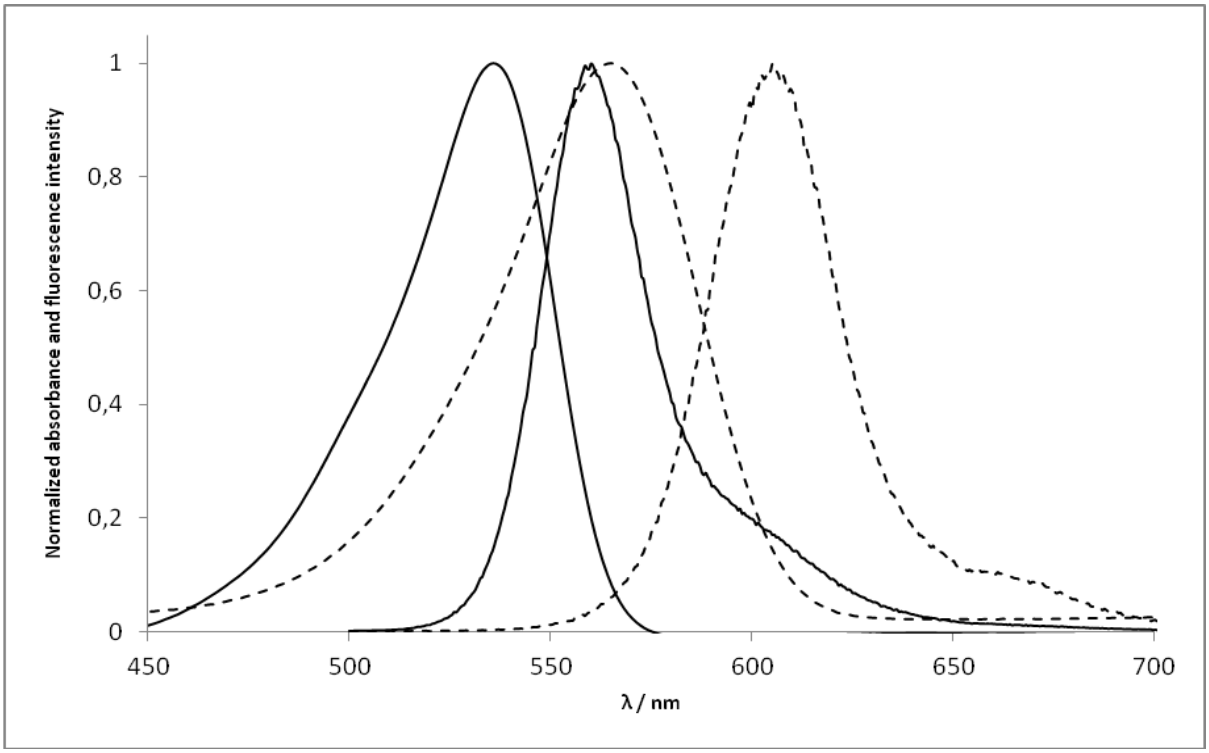


Figure S3. Normalized absorption and fluorescence emission profiles of **3i** (dashed) and **5d** (solid) in phosphate buffer at pH 7.4.

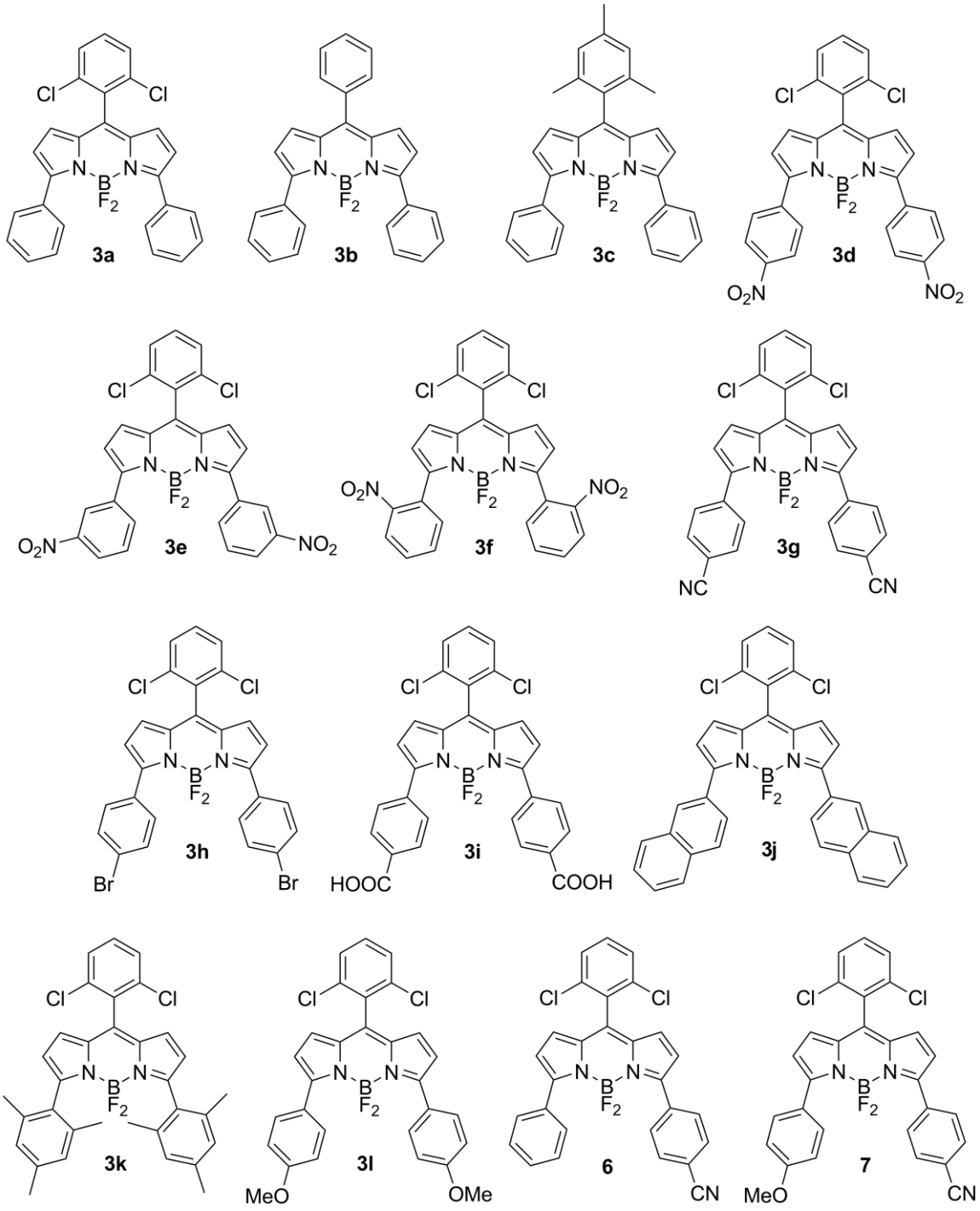


Chart S1. Structures of 3,5-diarylBODIPYs **3**, **6**, and **7**.

Table S4. Spectroscopic data and fluorescence quantum yields Φ of 3,5-diarylBODIPYs **3**, **6**, and **7** as a function of solvent. The solvents are listed from top to bottom according to increasing refractive index *n*.

Compound	Solvent	λ_{abs}(max) / nm	λ_{em}(max) / nm	$\Delta\bar{\nu}$ / cm^{-1}	$fwhm_{abs}$ / cm^{-1}	$fwhm_{em}$ / cm^{-1}	Φ
3a[a]	MeOH	565	596	921	1498	977	0.85 ± 0.02
	MeCN	561	597	1075	1544	1019	0.887 ± 0.006
	EtOAc	566	598	945	1454	975	0.901 ± 0.005
	THF	571	602	902	1431	942	0.894 ± 0.006
	Toluene	573	605	923	1451	963	0.901 ± 0.005
3b[a]	MeOH	550	583	1029	1601	1070	0.165 ± 0.002
	MeCN	546	583	1162	1631	1090	0.154 ± 0.002
	EtOAc	551	585	1055	1540	1042	0.195 ± 0.005
	THF	555	588	1011	1530	1030	0.200 ± 0.002
	Toluene	558	591	1001	1502	1026	0.336 ± 0.006
3c	MeOH[b]	552	582	934	1498	900	0.35 ± 0.01
	MeCN[b]	548	582	1051	1619	989	0.54 ± 0.03
	EtOAc[b]	553	584	960	1559	944	0.59 ± 0.03
	THF[c]	557	586	888	1466	931	0.84 ± 0.03
	Toluene[c]	559	589	911	1491	940	0.94 ± 0.02
3d	MeOH[c]	572	611	1131	1843	1031	0.69 ± 0.01
	MeCN[c]	570	613	1217	1850	1053	0.74 ± 0.02
	EtOAc[c]	573	613	1139	1768	1017	0.60 ± 0.01
	THF[c]	579	617	1079	1799	1038	0.47 ± 0.03
	Toluene[c]	579	618	1090	1698	1007	0.68 ± 0.04
3e	MeOH[c]	559	592	997	1656	959	0.91 ± 0.01
	MeCN[b]	558	593	1051	1526	957	0.82 ± 0.01
	EtOAc[c]	561	593	955	1680	981	0.87 ± 0.01
	THF[c]	564	596	938	1493	986	0.76 ± 0.03
	Toluene[c]	568	600	939	1506	986	0.82 ± 0.03
3f	MeOH[b]	532	559	918	994	—[e]	—[e]
	MeCN[b]	531	554	766	994	—[e]	—[e]
	EtOAc[b]	533	568	1141	1057	1499	0.01 ± 0.01
	THF[b]	535	568	1094	1049	—[e]	—[e]
	Toluene[b]	536	575	1258	1008	1441	0.03 ± 0.01
3g	MeOH[c]	568	602	981	1673	978	0.86 ± 0.01
	MeCN[c]	565	602	1081	1819	1007	0.85 ± 0.01
	EtOAc[c]	570	604	994	1564	988	0.88 ± 0.02
	THF[c]	575	609	957	1570	987	0.67 ± 0.01
	Toluene[c]	576	612	1036	1626	1006	0.72 ± 0.05
3h	MeOH[c]	571	604	950	1587	960	0.86 ± 0.02
	MeCN[c]	568	604	1036	1835	1015	0.90 ± 0.01
	EtOAc[c]	572	604	926	1547	984	0.88 ± 0.03
	THF[c]	577	609	911	1682	1027	0.48 ± 0.03
	Toluene[c]	580	612	902	1538	960	0.74 ± 0.03
3i	MeOH[c]	574	607	954	1638	964	0.79 ± 0.01
	MeCN[c]	567	604	1067	1870	1004	0.72 ± 0.02
	EtOAc[c]	572	604	913	1457	999	0.83 ± 0.01
	THF[c]	577	610	931	1493	997	0.69 ± 0.05

	Toluene	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]
	H_2O[b,f]	565	605	1157	1854	997	0.37 ± 0.02
3j	MeOH[c]	587	625	1023	1902	1011	0.70 ± 0.02
	MeCN[c]	582	626	1208	1895	1047	0.61 ± 0.01
	EtOAc[c]	588	626	1032	1829	996	0.54 ± 0.02
	THF[c]	593	630	984	1682	1022	0.73 ± 0.03
	Toluene[c]	594	632	1006	1670	980	0.56 ± 0.01
3k	MeOH	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]
	MeCN[b]	525	540	512	802	1136	0.90 ± 0.05
	EtOAc[b]	525	541	546	799	1034	0.91 ± 0.01
	THF[b]	526	543	604	833	1189	0.82 ± 0.05
	Toluene[b]	529	544	530	752	1147	0.98 ± 0.03
3l[a]	MeOH	594	632	1012	1727	1000	0.859 ± 0.007
	MeCN	590	635	1201	1806	1090	0.928 ± 0.009
	EtOAc	596	633	981	1664	961	0.94 ± 0.01
	THF	600	637	968	1615	971	0.935 ± 0.008
	Toluene	603	637	885	1582	947	0.954 ± 0.008
6	MeOH[c]	566	599	973	1586	978	0.94 ± 0.03
	MeCN[c]	563	597	1019	1868	1006	0.70 ± 0.01
	EtOAc[c]	568	599	911	1575	988	0.86 ± 0.04
	THF[c]	573	604	903	1581	975	0.71 ± 0.04
	Toluene[c]	574	606	920	1638	992	0.71 ± 0.01
7	MeOH[c]	582	619	1014	2044	1007	0.50 ± 0.04
	MeCN[c]	579	619	1123	2024	1056	0.49 ± 0.04
	EtOAc[c]	585	619	947	1996	991	0.52 ± 0.01
	THF[c]	590	623	904	1809	1016	0.42 ± 0.02
	Toluene[c]	591	625	927	1856	945	0.54 ± 0.03

[a] Reported previously.[5] [b] Φ determined vs rhodamine 101 in ethanol (Φ_r = 0.96) as a reference.[3a] [c] Φ determined vs rhodamine 6G in ethanol (Φ_r = 0.95) as a reference.[3b] [d] The solubility of the product is too limited in this solvent. [e] The compound is not fluorescent. [f] Aqueous phosphate buffer at pH 7.4.

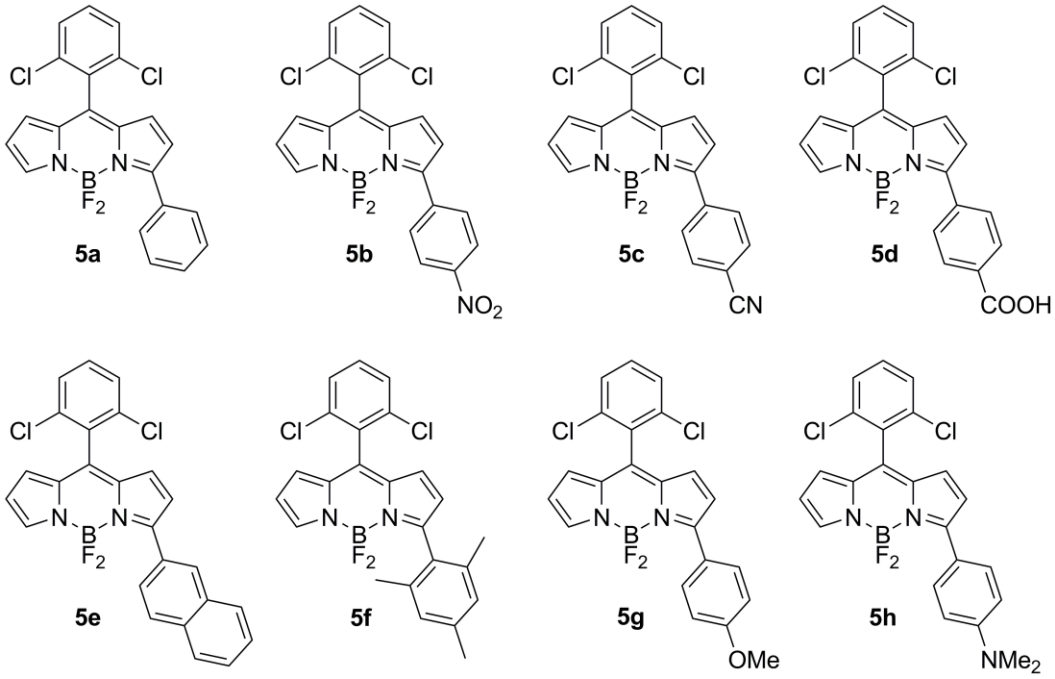


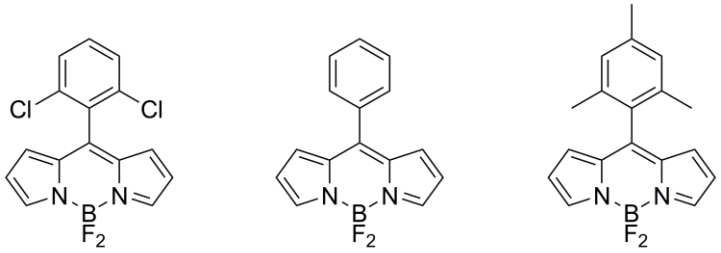
Chart S2. Structures of 3-arylBODIPYs **5**.

Table S5. Spectroscopic data and fluorescence quantum yields Φ of 3-arylBODIPYs **5** as a function of solvent. The solvents are listed from top to bottom according to increasing refractive index *n*.

Compound	Solvent	λ_{abs}(max) / nm	λ_{em}(max) / nm	$\Delta\bar{\nu}$ / cm^{-1}	$fwhm_{abs}$ / cm^{-1}	$fwhm_{em}$ / cm^{-1}	Φ
5a[a]	MeOH	537	556	636	1281	1020	0.858 ± 0.006
	MeCN	536	556	671	1305	1037	0.884 ± 0.008
	EtOAc	539	558	632	1198	1003	0.89 ± 0.02
	THF	542	561	625	1208	985	0.88 ± 0.01
	Toluene	545	565	650	1237	1002	0.8960 ± 0.005
5b	MeOH[b]	541	564	754	1648	954	0.63 ± 0.04
	MeCN[b]	540	564	788	1578	954	0.93 ± 0.01
	EtOAc[b]	543	565	717	1674	922	0.54 ± 0.03
	THF[b]	547	569	715	1506	940	0.59 ± 0.01
	Toluene[b]	548	573	789	1532	929	0.65 ± 0.03
5c	MeOH[b]	539	559	681	1405	890	0.94 ± 0.04
	MeCN[b]	537	560	749	1410	907	0.79 ± 0.02
	EtOAc[b]	541	561	651	1432	889	0.66 ± 0.06
	THF[b]	544	565	668	1305	878	0.72 ± 0.06
	Toluene[b]	546	568	709	1363	926	0.73 ± 0.01
5d	MeOH[b]	542	561	633	1389	899	0.85 ± 0.01
	MeCN[b]	539	559	656	1405	924	0.84 ± 0.05
	EtOAc[b]	542	561	625	1319	917	0.85 ± 0.02
	THF[b]	545	566	673	1263	906	0.35 ± 0.03
	Toluene[b]	548	568	667	1390	924	0.74 ± 0.02
	H_2O[b,d]	536	560	800	1569	969	0.85 ± 0.02
5e	MeOH[b]	549	572	740	1600	972	0.64 ± 0.01
	MeCN[b]	547	572	799	1612	1022	0.77 ± 0.01
	EtOAc[b]	551	573	704	1704	1114	0.78 ± 0.01

	THF[c]	554	576	682	1360	946	0.75 ± 0.03
	Toluene[c]	557	580	697	1482	964	1.00 ± 0.01
5f[a]	MeOH	516	531	547	861	1273	0.820 ± 0.007
	MeCN	515	531	585	902	1287	0.846 ± 0.005
	EtOAc	517	532	545	866	1287	0.848 ± 0.005
	THF	518	534	578	872	1314	0.872 ± 0.005
	Toluene	521	537	572	831	1304	0.885 ± 0.005
5g[a]	MeOH	553	575	692	1587	1085	0.82 ± 0.01
	MeCN	552	577	785	1631	1161	0.854 ± 0.009
	EtOAc	555	577	687	1449	1053	0.86 ± 0.02
	THF	558	579	650	1409	1061	0.861 ± 0.009
	Toluene	562	583	641	1388	1015	0.875 ± 0.006
5h	MeOH[c]	608	—[e]	—[e]	2344	—[e]	—[e]
	MeOH + $HClO_4$[b,f]	535	554	641	1382	927	0.54± 0.01
	MeCN[c]	608	—[e]	—[e]	3483	—[e]	—[e]
	EtOAc[c]	608	—[e]	—[e]	2255	—[e]	—[e]
	THF[c]	612	629	449	2232	1229	0.09 ± 0.02
	Toluene[c]	619	665	1123	2154	1510	0.16 ± 0.02

[a] Reported previously.[5] [b] Φ determined vs rhodamine 101 in ethanol (Φ_r = 0.96) as a reference.[3a] [c] Φ determined vs rhodamine 6G in ethanol (Φ_r = 0.95) as a reference.[3b] [d] Aqueous phosphate buffer at pH 7.4. [e] The compound is not fluorescent. [f] Methanol with excess $HClO_4$ was used.



1a **1b** **1c**

Chart S3. Structures of the starting materials **1**.

Table S6. Spectroscopic data and quantum yields Φ of the starting BODIPY materials **1**. The solvents are listed from top to bottom according to increasing refractive index *n*.

Compound	Solvent	λ_{abs}(max) / nm	λ_{em}(max) / nm	$\Delta\bar{\nu}$ / cm^{-1}	$fwhm_{abs}$ / cm^{-1}	$fwhm_{em}$ / cm^{-1}	Φ
1a[5]	MeOH	509	522	489	897	1224	0.801 ± 0.006
	MeCN	508	522	528	914	1261	0.81 ± 0.01
	EtOAc	510	523	487	887	1223	0.820 ± 0.008
	THF	512	526	520	886	1223	0.82 ± 0.02
	Toluene	515	530	550	873	1273	0.843 ± 0.005
1b	Toluene	504[6]	518[6]				0.062[6], 0.053[7]
1c[8]	Toluene	503	517				0.93

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